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PHILOSOPHICAL MAGAZINE

AND

JOURNAL OF SCIENCE.

CONDUCTED BY

SIR OLIVER JOSEPH LODGE, D.Sc., LL.D., F.R.S.
SIR JOSEPH JOHN THOMSON, O.M., M.A., Sc.D., LL.D., F.R.S.
JOHN JOLY, M.A., D.Sc., F.R.S., F.G.S.
RICHARD TAUNTON FRANCIS
AND
WILLIAM FRANCIS, F.L.S.

"Nec aranearum sane textus ideo melior quia ex se fila gignunt, nec noster vilior quia ex alienis libamus ut apes." JUST. LIPS. *Polit.* lib. i. cap. 1. Not.

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"Meditationis est perscrutari occulta; contemplationis est admirari perspicua .... Admiratio generat quæstionem, quæstio investigationem, investigatio inventionem."—*Hugo de S. Victore.*

——" Cur spirent venti, cur terra dehiscat,
Cur mare turgescat, pelago cur tantus amaror.
Cur caput obscura Phœbus ferrugine condat,
Quid toties diros cogat flagrare cometas,
Quid pariat nubes, veniant cur fulmina cœlo.
Quo micet igne Iris, superos quis conciat orbes
Tam vario motu."

J. B. Pinelli ad Mazonium.

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ERRATA.

Page 177, vol. 49, line 12, for ct_0 read vt_0.

" " " " 17, for $0<x<ct_0$ read $0<x<vt_0$.

The formula on page 872, vol. 50, line 28 should read:—

$$N^2=4 \sin \tfrac{1}{2}(\alpha+\beta+\gamma) \sin \tfrac{1}{2}(-\alpha+\beta+\gamma)$$
$$\sin \tfrac{1}{2}(\alpha-\beta+\gamma) \sin \tfrac{1}{2}(\alpha+\beta-\gamma).$$

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[SIXTH SERIES.]

JULY 1925.

I. *A Method for Increasing the Working Range of an Oscillograph.* By C. E. WYNN-WILLIAMS, *M.Sc., University Research Student, University College of North Wales, Bangor* *.

[Plate I.]

WITH all types of oscillograph which employ a mechanical moving system as the medium between the quantity to be studied (which actuates the instrument) and the record, a great disadvantage arises from the fact that the usefulness of the instrument is limited by the frequency range over which accurate results are obtainable. The extent of this range depends upon (1) the type of oscillation to be studied, (2) the maximum error permissible, (3) the natural frequency and damping of the instrument. When the oscillograph (which, for the present purpose, is supposed to be a simple mechanical oscillatory system, having only one frequency of vibration, $\frac{n}{2\pi}$, and capable of being made to execute forced oscillations by the quantity to be examined) is adjusted so that the system is just aperiodic (*i. e.* damping factor $k=2n$), thus rendering free oscillation of the system impossible, it can be shown that the amplitude scale (*i. e.* the amplitude of oscillation per unit force) diminishes as the frequency increases. If the natural periodicity of the instrument $=n$, and the amplitude scale for a steady deflexion $=100$, then for an oscillation of periodicity of $0{\cdot}1n$ the amplitude scale will be 99·3, and for a periodicity of $0{\cdot}2n$, 96·0, thus

* Communicated by Prof. E. Taylor Jones, D.Sc.

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introducing errors of 0·7 per cent. and 4·0 per cent. respectively. As the frequency still further rises, the error increases, until, at the natural frequency of the instrument, it is as large as 50 per cent. Evidently, then, if the nature of the curve makes it desirable for all frequencies to be recorded with uniform amplitude scales, the range of frequencies over which accurate results are obtainable is very small, being, as before mentioned, from 0 to $0{\cdot}1n$ for errors not exceeding 0·7 per cent., and from 0 to $0{\cdot}2n$ for a 4·0 per cent. error. With certain curves, however (*i. e.* pure sine waves with or without slight damping), the error is of no account, provided that the amplitude scale for that particular frequency is known.

The difficulty of obtaining true records at high frequencies is evident when it is realized that the frequency of the instrument must be from five to ten times that of the most rapid oscillation to be recorded, and that the natural frequency of most mechanical oscillographs rarely exceeds about 10,000 vibrations per second.

It was thought that some means might be found for compensating the instrument, by reducing the amplitude scale for the lower frequencies, and increasing it for the higher, so that the amplitude scale would tend to vary less with the frequency than in the uncompensated instrument, thus enabling the frequency range to be increased. This might be done by subjecting the instrument to only a fraction of the quantity to be examined, and making this fraction a function of the frequency which would be large at high frequencies and small at low frequencies. The form of function required to secure compensation can best be determined by mathematical analysis. Some indication of the best way of applying the method in practice will also be made evident by this treatment of the problem.

Theory

The equation of motion of the system is

$$\frac{d^2x}{dt^2} + k\frac{dx}{dt} + n^2x = \mathrm{F},$$

where x = displacement, k = damping factor, n = periodicity (undamped), and F = force actually applied to the instrument, per unit of inertia. This may be written as

$$(\mathrm{D}^2 + k\mathrm{D} + n^2)x = \mathrm{F},$$

where D stands for the operator $\frac{d}{dt}$.

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F will, in general, be a periodic function, or a combination of such functions (*i. e.* a Fourier series) such as

$$F = \sum_{1}^{\infty} F_m \epsilon^{-\mu t} \begin{Bmatrix} \sin \\ \cos \end{Bmatrix} mpt.$$

For the present purpose, however, it will be assumed that F is only a single undamped oscillation. In this case the equation becomes

$$(D^2 + kD + n^2)x = F_0 \sin pt,$$

the solution of which is

$$x = A\epsilon^{-\frac{k}{2}t} \sin\left(\sqrt{n^2 - \frac{k^2}{4}} + \alpha\right) + \frac{F_0 \sin pt}{D^2 + kD + n^2}.$$

The first term (the complementary function) is aperiodic, provided that k is not less than $2n$, for which reason k is always made equal to or greater than $2n$ in an instrument of this kind. In any case, the first term tends to zero as t increases. We are then left with a solution,

$$x = \frac{F_0 \sin pt}{D^2 + kD + n^2},$$

which, on expansion, becomes

$$x = \frac{F_0 \sin (pt - \phi)}{\sqrt{(n^2 - p^2)^2 + k^2 p^2}},$$

where

$$\tan \phi = \frac{kp}{n^2 - p^2}.$$

This shows that the amplitude scale

$$\frac{1}{\sqrt{(n^2 - p^2)^2 + k^2 p^2}}$$

is a function of the frequency, and that the phase of the record lags behind that of the force by an angle

$$\phi = \tan^{-1} \frac{kp}{(n^2 - p^2)}.$$

The problem is, therefore, to make (1) the amplitude scale constant, or as nearly constant as possible, so that the amplitude of the record is a true scale representation of the magnitude of the force at all frequencies, and (2) to make the phase angle as nearly equal to zero as possible, so that the various components of the force are recorded in correct phase

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relation to one another. This can be done in the following way. So far we have supposed that the instrument is subjected to the whole of the applied force. Suppose, now, that some link is introduced between the force and the instrument (*e. g.* a shunt resistance, potentiometer, or volt-box, etc.) which will tap off a fraction of the force and apply it to the instrument. It is conceivable that the link could be so constructed that the magnitude of the fraction would depend upon the frequency, and that the relative phases of the force and its fraction could be changed. Let this fraction be ρ. Then, if the force to be examined (to which the link is submitted) is equal to A, the fraction which will be passed on to the oscillograph will be ρA. Replacing F by ρA in the expression for x, we get

$$x = \frac{\rho A}{D^2 + kD + n^2}.$$

What is required for perfect compensation is that the expression for x should be of the form $x = \sigma A$, where σ is a constant. Hence, by comparing the two expressions, we see that

$$\frac{\rho A}{D^2 + kD + n^2} = \sigma A.$$

Since σ is a constant, and A a function of p, no matter what form, it is evident that the fraction ρ must be equal to the operator $\sigma(D^2 + kD + n^2)$. The properties of such an operator may be made evident by supposing that A is a single undamped oscillation,

$$A = A_0 \sin pt.$$

Hence

$$\rho A = \rho A_0 \sin pt = \sigma(D^2 + kD + n^2) A_0 \sin pt,$$

which on expanding becomes

$$\rho A = \sigma \sqrt{(n^2 - p^2)^2 + k^2 p^2}\, A_0 \sin(pt + \phi),$$

where

$$\tan \phi = \frac{kp}{(n^2 - p^2)}.$$

This represents the force F applied to the instrument, so that we now have

$$x = \frac{F}{D^2 + kD + n^2} = \frac{\sigma \sqrt{(n^2 - p^2)^2 + k^2 p^2}\, A_0 \sin\{(pt + \phi) - \phi\}}{\sqrt{(n^2 - p^2)^2 + k^2 p^2}}$$

$$= \sigma A_0 \sin pt.$$

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From this it will be seen that x, the displacement, is a true scale representation of the force at all frequencies, and, further, that the record is in phase with the force, showing that proper compensation has been obtained. This may be explained by saying that the link *multiplies* the amplitude by $\sqrt{(n^2-p^2)^2+k^2p^2}$ and *advances* the phase by an angle ϕ, while the oscillograph *divides* the amplitude by $\sqrt{(n^2-p^2)^2+k^2p^2}$ and *retards* the phase by ϕ, thus giving a constant amplitude scale and zero phase change for all frequencies.

It is not necessary that A should always be of the form $A_0 \sin pt$ for compensation to take place. For, by substituting ρA for F, we get

$$x = \frac{F}{(D^2+kD+n^2)} = \frac{\rho A}{(D^2+kD+n^2)}$$

$$= \frac{\sigma A(D^2+kD+n^2)}{(D^2+kD+n^2)} = \sigma A,$$

showing that compensation is independent of the form of A. The assumption that $A = A_0 \sin pt$ was made in order that it might be ascertained what properties the link should possess, and so give some indication as to its practical form.

Method of Applying Compensation.

As a specific example, suppose we have an electrostatic oscillograph of small capacity, and satisfying the equation

$$(D^2+kD+n^2)x = F$$

(F in this case being the potential applied to the instrument), and we require to compensate it. The amplitude x is given by

$$x = \frac{F}{D^2+kD+n^2}.$$

We require it to be of the form $x = \sigma E$, where E = the voltage to be examined. To make this so, F must be of the form

$$F = (D^2+kD+n^2)E.$$

The problem is then to find a means of tapping off this fraction of the voltage.

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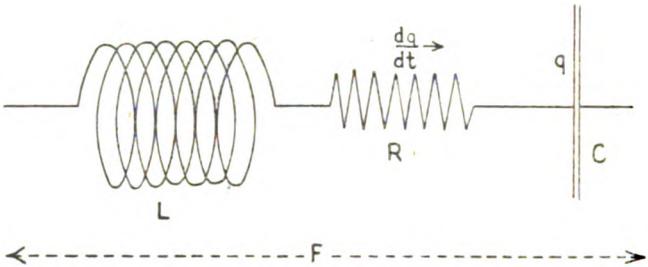
Suppose we have a circuit as shown in fig. 1, consisting of an inductance L, a resistance R, and a condenser C, all in

Fig. 1.



series. Let the potential applied to the ends of the circuit be F, and the displaced charge at any moment $=q$, so that the current $=\frac{dq}{dt}$ or Dq. Then

$$F=\left(LD^2+RD+\frac{1}{C}\right)q.$$

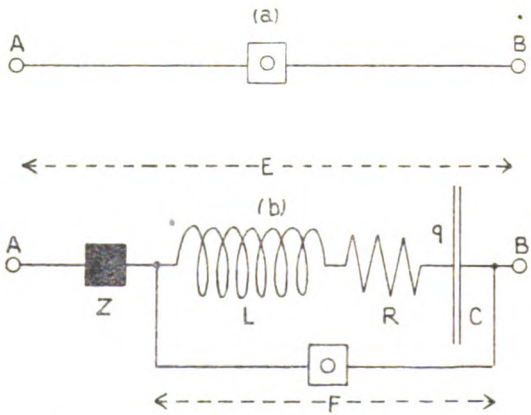
Suppose, now, that L, R, and C be so chosen that

$$\frac{R}{L}=k, \quad \text{and} \quad \frac{1}{LC}=n^2;$$

then

$$F=\left(D^2+\frac{R}{L}D+\frac{1}{LC}\right)qL \quad \text{or} \quad F=(D^2+kD+n^2)qL$$

Fig. 2.



Let there be a difference of potential E between the two terminals A and B (fig. 2 (*a*)), which potential it is required to

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examine. Under ordinary circumstances the oscillograph O would be connected as shown. Instead of doing this, however, let the instrument be connected as shown in fig. 2 (*b*). The terminals A and B are connected by an inductance L, a resistance R, a condenser C, and the apparatus Z (shown by a black square), all in series, while the oscillograph is connected across L, R, and C. The nature of the apparatus Z has to be such that the displacement charge q in the circuit is rendered proportional only to the voltage E (*i. e.* $q=\sigma E$), and is not a function of p other than a periodic function of the same form as E.

The instrument is now submitted to the back E.M.F. of the combination L, R, and C. Denoting this by F, we get

$$x = \frac{F}{(D^2+kD+n^2)} = \frac{(D^2+kD+n^2)qL}{(D^2+kD+n^2)} = \sigma EL.$$

From this it will be seen that, if the apparatus Z keeps the displacement charge in the circuit proportional only to E, compensation is provided, for *x is now proportional to* E, no matter what frequency is dealt with.

The next step is to investigate the nature of the required apparatus Z, which, generally, we may consider to have inductance L_1, resistance R_1, and capacity C_1. Writing down the expression for q, we get

$$q = \frac{E}{\left(LD^2+RD+\frac{1}{C}\right)+\left(L_1D^2+R_1D+\frac{1}{C_1}\right)}$$

Bearing in mind the fact that L, R, and C have already been determined, and that the presence of the operator D indicates a function of p in the solution, it is evident that it is impossible, by means of such a system, to make q independent of p, but that an approximation to it can be obtained if L_1 and R_1 are both zero and C_1 very small. When L_1 and $R_1=0$,

$$q = \frac{E}{LD^2+RD+\left(\frac{1}{C}+\frac{1}{C_1}\right)}.$$

This indicates that apparatus Z should be a condenser. In practice, however, it has been found necessary to include in the circuit a resistance R_1, as the whole system must be rendered aperiodic from an electrical point of view, which is done by suitably adjusting the value of R_1. The inclusion

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of this resistance, however, makes q more dependent upon p than it otherwise would be.

The form of compensation given by this arrangement may be seen by writing down the equations for the system:

$$q = \frac{E}{\left\{ LD^2 + (R+R_1)D + \left(\frac{1}{C} + \frac{1}{C_1}\right) \right\}},$$

$$F = \left(LD^2 + RD + \frac{1}{C}\right) q$$

$$= \frac{\left(LD^2 + RD + \frac{1}{C}\right) E}{\left\{ LD^2 + (R+R_1)D + \left(\frac{1}{C} + \frac{1}{C_1}\right) \right\}},$$

$$x = \frac{F}{(D^2 + kD + n^2)} = \frac{\left(LD^2 + RD + \frac{1}{C}\right) E}{\left\{ LD^2 + (R+R_1)D + \left(\frac{1}{C} + \frac{1}{C_1}\right) \right\}} \times \frac{1}{(D^2 + kD + n^2)}.$$

As it has been arranged that $\frac{R}{L} = k$, and that $\frac{1}{LC} = n^2$, we get

$$x = \frac{E}{\left\{ D^2 + \left(k + \frac{R_1}{L}\right) D + \left(n^2 + \frac{1}{LC_1}\right) \right\}},$$

or, putting

$$\frac{R_1}{L} = k_1 \quad \text{and} \quad \frac{1}{LC_1} = n_1^2$$

to correspond with k and n^2,

$$x = \frac{E}{\{D^2 + (k+k_1)D + (n^2 + n_1^2)\}}.$$

The oscillograph therefore behaves as if it had a periodicity $\sqrt{n^2 + n_1^2}$ instead of n, and a damping factor $k + k_1$ instead of k. We have *virtually increased the natural frequency* of the system, thus giving the instrument a greater working range of frequencies for compound oscillations.

This may be made clearer by the aid of a graph. Assuming the instrument to be just aperiodic ($k = 2n$) and

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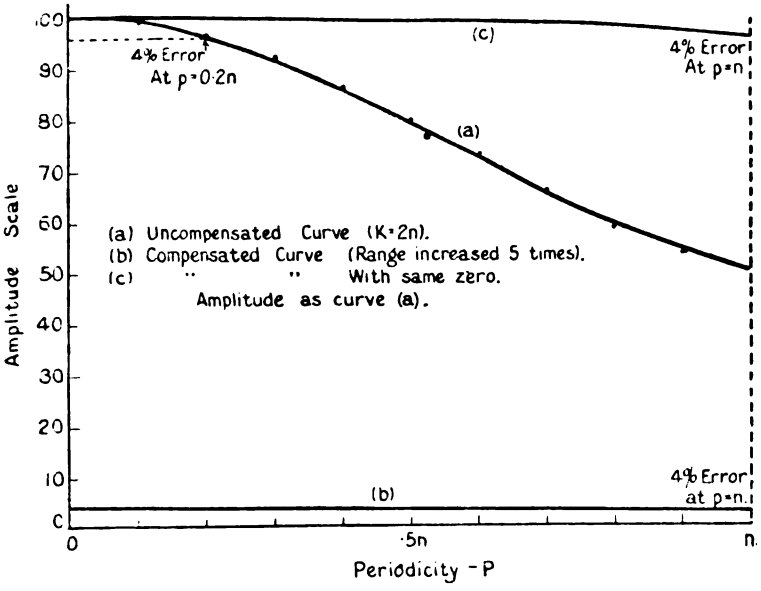
not compensated, the amplitude scale varies with the frequency as shown by curve (a), fig. 3. Now make $n_1^2 = 24n^2$, so that N, the virtual natural frequency, $= \sqrt{n^2 + 24n^2} = 5n$, and make $k_1 = 8n$, so that K, the virtual damping factor, $= 10n = 5k$. This may be done by making $C_1 = \frac{1}{24}C$ and $R_1 = 4R$; L, R, and C having been previously adjusted so that

$$\frac{R}{L} = k \quad \text{and} \quad \frac{1}{LC} = n^2.$$

Fig. 3.



The amplitude scale will now be the same as that of an oscillograph of periodicity $= 5n$ and damping factor $= 10n$, and will be represented by curve (b), fig. 3. It will be observed that the slope of this latter curve is much more gentle than that of the former, although the amplitude scale for a steady deflexion is much less (*i. e.* in (a) the steady deflexion for unit applied potential is $\frac{1}{n^2}$, while in curve (b) the corresponding deflexion is

$$\frac{1}{n^2 + n_1^2} = \frac{1}{25n^2},$$

a ratio of 25: 1). Curve (c) shows the compensated curve (b)

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magnified 25 times so as to have the same zero amplitude scale as curve (*a*) the uncompensated one. It will be observed that curve (*a*) falls much more rapidly than curves (*b*) or (*c*). A 4 per cent. error, for example, would be involved within the range $p=0$ to $p=0{\cdot}2n$ for curve (*a*), while the range in which the same error would be incurred in curves (*b*) and (*c*) is from 0 to n, or from 0 to 0·2N. The working range, in this case, has therefore been increased five times. The sensitiveness, however, has been decreased twenty-five times. Hence, provided the decrease in sensitiveness can be overcome by some means (*e. g.* valve amplification of the voltage), it is clearly an advantage to compensate the system.

So far nothing has been said about the error introduced by ignoring the phase change for the various frequencies; it may be shown, however, that the phase lag is also compensated in a similar manner. For example, in the uncompensated system, the phase lag at $p=0{\cdot}2n$ is $\tan^{-1} 0{\cdot}4167$ or $22^\circ\, 37'$. In the compensated instrument this lag would only occur at a frequency of $p=n$ (or $p=0{\cdot}2\mathrm{N}$), showing that the working range has in this case been increased five times.

Experimental Test of the Theory.

In order to test the above theory, an oscillograph is required which (1) is electrostatic, (2) is very sensitive, so as to enable reasonable amplitudes to be obtained with large compensations, and (3) satisfies the equation

$$\mathrm{F} = (\mathrm{D}^2 + k\mathrm{D} + n^2)x.$$

Fortunately it is not necessary that it should also have a high natural frequency, as for the present purpose it is only required to show that a low natural frequency can be virtually raised by compensation. As most electrostatic oscillographs are insensitive at low voltages, it was decided to construct an artificial electrostatic oscillograph by using a current oscillograph in conjunction with a valve.

In fig. 4, O represents a current oscillograph, inserted in the plate circuit of an amplifying valve. This oscillograph is supposed to be sensitive enough to respond to the small changes in the plate current of the valve (of the order of a few milliamperes) caused by any variation of the potential of the grid. In this way a current oscillograph may be made to record potential variations. Two conditions must, however, be observed to obtain true results. (1) The voltage applied to the grid must be such that the plate current in

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Fig. 4.

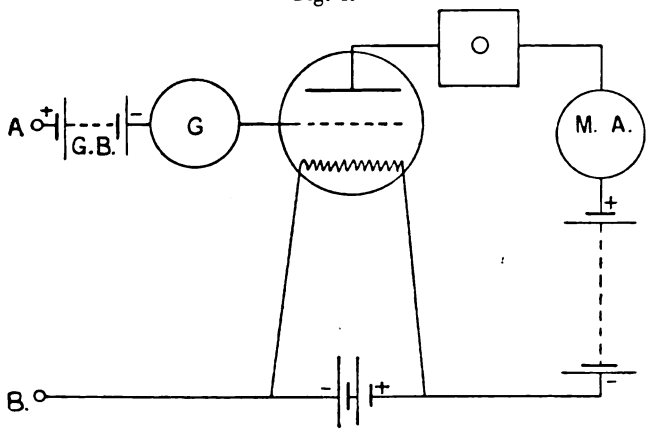
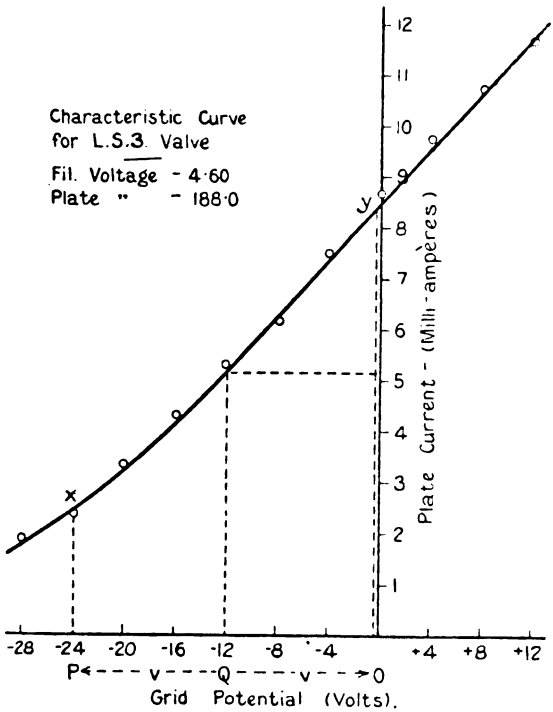


Fig. 5.



the valve is always represented by the straight portion of its characteristic curve (*i. e.* to the right of the point *x* in fig. 5),

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and (2) the grid current must always be zero. Hence it will be observed that the only voltages that can be applied to the grid must lie between zero and the value corresponding to that just above where the plate current curve begins to bend—*i. e.* from P to O (fig. 5). These are all negative values. The mean working position will be at Q, half-way between P and O. Calling PQ (=QO) v, we see that, by superimposing a steady voltage of $-v$ on the grid by means of the grid battery GB (fig. 4), any voltage oscillation whose peak value does not exceed v will be passed on by the valve and transformed into a similar current oscillation, without distortion, which will be recorded by the current oscillograph. As the grid current is kept at zero, the "input" side of the valve (*i. e.* the grid and filament terminals) will represent the terminals of a perfectly electrostatic instrument of small capacity—at any rate, so far as concerns any apparatus to which the grid is connected. The sensitiveness of the system will depend upon (1) the slope of the plate current curve, and (2) the sensitiveness of the oscillograph O.

A very convenient, though not ideal, oscillograph was constructed from a Brown's "A" type telephone earpiece*. This was of resistance 4000 ohms, and had a vibrating steel reed attached to a conical diaphragm as an armature. The diaphragm was removed, and to the free end of the reed a thin sheet-brass extension was attached, bent as shown in fig. 6. Between this and a fixed brass plate, a small mirror about 1 mm. square was clamped, the surfaces of both the extension and the plate being covered with thin slips of cork where the mirror was held. This constituted an optical lever which magnified the movement of the free end of the reed. As the distance between the reed and the magnet can be adjusted by means of a screw in this type of telephone, the sensitiveness could be conveniently varied. To supply the necessary damping, a thick brass bridge was attached to the magnet, just under the extension of the reed. Through the centre of this a screw passed, carrying at its upper end a small platform parallel to the extension, and between these two surfaces some viscous liquid was introduced (see fig. 6). It was found necessary to bend the extension back upon itself to prevent the liquid from creeping on to the reed and into the space between the reed and the pole-pieces. The whole was mounted in a universal joint to facilitate the centering of the light-spot.

* The writer is indebted to Mr. W. E. Williams, B.Sc., for this suggestion.

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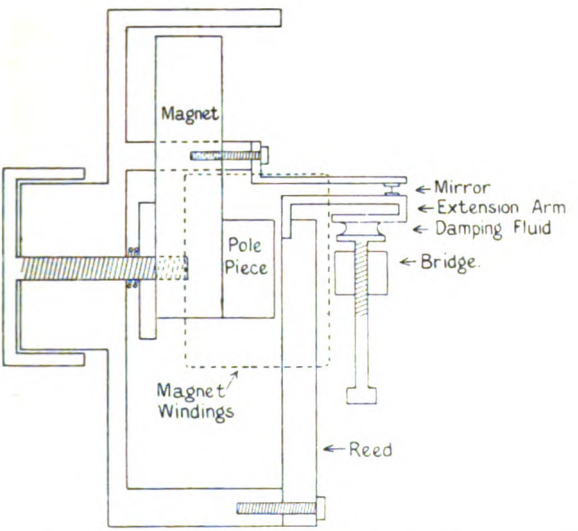
A beam of light from a pinhole, upon which the crater of an arc lamp was focussed, fell on the mirror and, after reflexion, on to a revolving concave mirror, which caused the light-spot to move in a horizontal direction across a photographic plate or a ground-glass screen placed at the distance for correct focus. The oscillograph was so arranged that when working it deflected the beam in a vertical direction. By means of a mirror attached to the prong of a tuning-fork placed near the oscillograph a second spot was made to fall on the screen, just under the first, thus giving a time-scale independent of the velocity of the light-spots across the plate.

Fig. 6.



The valve employed was a Marconi L.S. 3, as used for power amplification. In all cases the filament voltage was kept at 4·6 volts and the plate voltage at 188. It was found impracticable to use the ordinary power-mains for the H.T. supply, owing to the presence of a commutator ripple which appeared in the oscillograms. Accordingly four ordinary 60-volt high-tension batteries connected in series were employed, and were found to be quite satisfactory. A milliammeter was inserted in the plate circuit, and a sensitive table galvanometer, G, was connected in series with the grid to indicate the presence of any grid current. It was found that the inclusion of this galvanometer did

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not interfere with the working of the apparatus to any observable extent.

The first operation was to standardize the valve and oscillograph. A characteristic curve for the valve was taken in the usual manner, by applying various voltages to the grid and recording the corresponding values of the plate current. This was done with all the apparatus in position. The curve obtained is shown in fig. 5. The curve was taken again after the experiments were concluded, to see if it had altered in the meantime, but it was found not to have changed. From this curve the available voltage range that could be applied to the valve was determined. This extended from just above the lower bend marked x to just short of zero, giving a working range in this case of about 24 volts. The mean potential was therefore -12 volts. This indicated the voltage of the grid battery required, which was then inserted in the circuit.

In order to adjust the oscillograph, the light-spot was allowed to fall on the screen (the revolving mirror being kept stationary) and the adjusting screw altered until, on changing the potential of the grid from zero to -24 volts (thus moving it through its maximum working range), the spot travelled through as great a distance on the screen as possible. This ensured the maximum sensitiveness. To test whether or not the amplitude was a linear function of the grid voltage, the grid was subjected to alternating voltages (frequency about 50 cycles per second) by means of a potentiometer, and the amplitude of vibration of the spot observed for different voltages. The voltage was measured by means of an electrostatic voltmeter. It was found that the displacement of the spot on the screen was not quite symmetrical with respect to its zero position. This was to be expected, since a vibrating reed, acted upon on one side only by a magnetic field, was not a symmetrical arrangement. If, however, the magnet was not brought too close to the reed (*i. e.* if the system was not made quite as sensitive as it might have been), it was found that, although the amplitude was unsymmetrical with regard to the zero position, it was in all cases proportional to the voltage applied to the grid within the limits of experimental error. When a suitable position for the magnet had been found, it was left set in that position during the whole of the subsequent experiments.

The natural frequency of vibration of the reed must be known. This was ascertained in two ways: (1) from the peak of the resonance curve, and (2) by photographing the free oscillations of the reed and measuring the curve.

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The first method was approximate only, and served as a check on the second. The amplitude of oscillation was observed while an alternating voltage from an oscillating valve was applied to the grid of the amplifying valve. The frequency of oscillation was raised, and the value found which corresponded to the maximum amplitude of vibration of the spot. This was the resonant frequency of the reed without damping. In the second method a switch actuated by the turn-table of the revolving mirror was arranged suddenly to alter the grid potential at the moment when the spot passed across the photographic plate. This caused the reed to vibrate in its own frequency, and from the oscillogram obtained the natural frequency was determined.

It was necessary to render the system aperiodic. This was done by introducing some viscous fluid between the platform and the extension (see fig. 6). Various fluids were tried—vaseline, castor oil, petroleum, syrup, and a mixture of vaseline and petroleum. The syrup was found to be the most suitable to work with. It was necessary, however, as already explained, to bend the extension back upon itself so as to form a trap for the syrup, to prevent it from creeping. By altering the distance between the platform and the extension the degree of damping could be varied.

The mirror was set revolving and the shape of the curve on the screen was observed (the switch worked by the mirror turn-table as before changing the grid potential suddenly at the moment when the spot passed across the screen), while the damping was varied. With a little care it was found possible to adjust the damping so that there was no trace of free oscillations present. The damping was kept at the minimum value necessary for this so as to ensure operating as near as possible to the curve corresponding to $k=2n$. (Later on, on examining the resonance curve, it was found that k had to be much greater than $2n$ to ensure aperiodicity for this particular instrument.) When the system was aperiodic, the shape of the curve for a sudden change of voltage approximated fairly well to its theoretical value, although the self-inductance of the windings of the magnet caused a slight lag. The lag, no doubt owing to the high resistance of the plate circuit of the valve, was, however, less than was expected.

The system being made aperiodic, an attempt was made to ascertain whether the resonance curve conformed to the theoretical shape of the curve corresponding to $k=2n$. This was done by subjecting the grid to alternating voltages of various frequencies supplied by either an alternator or an

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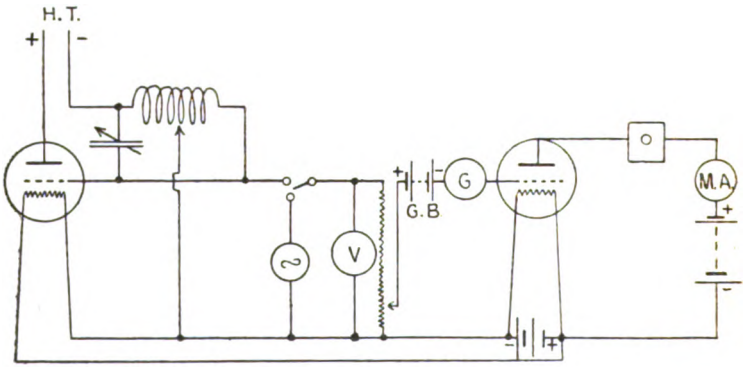
oscillating valve and measuring the amplitude of oscillation of the spot. For frequencies below 100 per second the alternator was used, and above that frequency the valve. In most cases the full voltage was found to be too much for the grid of the amplifying valve, whose working range, as has already been shown, was limited (0 to -24 volts) by the shape of its characteristic curve. A known fraction of the voltage was therefore tapped off by means of a divided megohm. Fig. 7 shows the connexions of the apparatus. The amplitude for steady voltage was found by replacing the alternator by the power-mains and taking readings for equal positive and negative values of potential.

Fig. 7.



On drawing the resonance curves, it was observed (1) that the damping was much greater than that given by $k=2n$, and (2) that a "hump" appeared in the curve at a frequency of about 700–800, although the system was supposed to be aperiodic. After a careful examination of the apparatus it was found that several portions of the telephone were constructed of rather thin material which might possibly have vibrated. Accordingly the whole was dismantled, and packing pieces of thick brass inserted where considered necessary. After reassembling, the preliminary operations of determining the natural frequency and making the system aperiodic had to be repeated. When the new resonance curve was plotted, it was found to be free from "humps," but the damping was still greater than expected. On calculating the values of the damping at various frequencies, by inserting in the formula the values of the amplitude scale read from the graph, it was found that the damping was not

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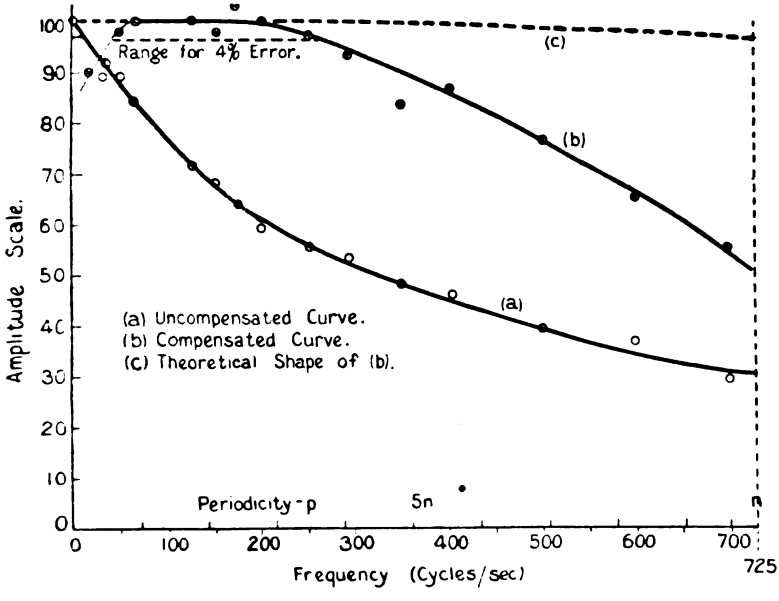
constant, but diminished as the frequency of the applied force increased. This was found to be so in all cases. Although the results were repeated with several damping liquids, and with various adjustments, it was found impossible to obtain a uniformly damped resonance curve, the only conclusion to be drawn from such a result being that the ordinary law of viscosity does not hold under the conditions obtaining in the experiment. For this reason it was decided to assume that the damping was constant over a short range, and to attempt to compensate for this range only, the average value of the damping factor over the range being taken as the value to be inserted in the formula for the determination of R. Fig. 8 (*a*) shows the resonance curve

Fig. 8.



dealt with in a particular case. The damping was taken as being equal to 6·60*n*. For effecting the compensation, an inductance, two condensers, and two resistances were required. The inductance in this case was part of the secondary winding of a small induction coil from which the core and primary coil had been removed. It had a resistance of 1756 ohms and an inductance of 1·150 henry, as measured by Rayleigh's method. It was necessary to connect this in

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series with a condenser, C (see fig. 9), of such a capacity that the two formed an oscillatory circuit of the same frequency as the reed, viz. 725·0. From the formula

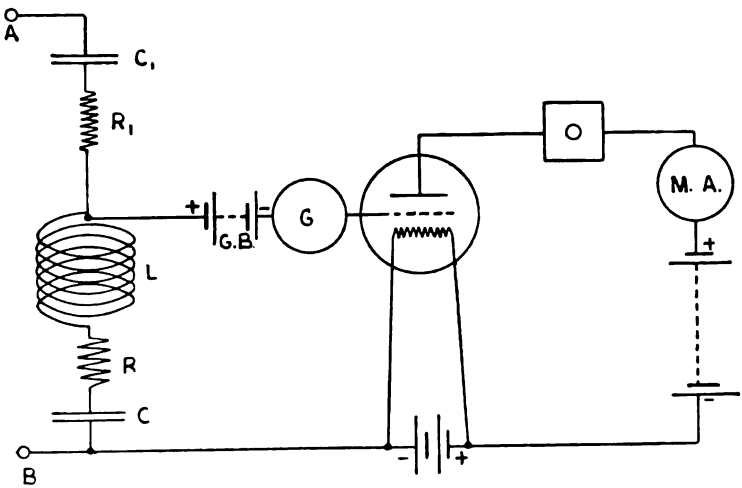
$$T = 2\pi\sqrt{LC} = \frac{1}{F}$$

we find

$$C = \frac{1}{4\pi^2F^2L} = \frac{1}{4\pi^2 \times 725^2 \times 1{\cdot}150} = 0{\cdot}04191 \text{ mfd.}$$

Accordingly condenser C was adjusted to this value.

Fig. 9.



The total resistance in this part of the circuit (L, R, and C) across which the valve was to be connected had now to be adjusted so that $\frac{R}{L} = k$. From this, taking k as equal to 6·60n (the value at the mean position in the range for which the instrument was to be compensated), R was found to be 34,570 ohms. This value included the resistance of the inductance (viz. 1756 ohms), so that an additional resistance of 32,814 ohms was required.

It then remained to adjust C_1 and R_1. In most of the experiments performed, and also in this particular case, it was endeavoured to increase the working range five times, as was done in the theoretical example for which the curves

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shown in fig. 3 were drawn. That is, C_1 had to be made equal to $\frac{C}{24}$, or 0·001746 mfd. Condenser C_1 consisted of a large air dielectric variable condenser having a maximum capacity of 0·0025 mfd. This was calibrated, and the capacity was set to the required value, due allowance being made for the zero error. Lastly, R_1 had to be so adjusted that the whole electrical system was aperiodic. The condition for this was that

$$\frac{R+R_1}{L} = K = 2N \quad \text{or} \quad R+R_1 = 10nL,$$

from which $R+R_1 = 52{,}390$ ohms. R being equal to 34,570 ohms, R_1 was 17,820 ohms.

This arrangement, when connected up, constituted the required link for effecting compensation. Theoretically the oscillograph should now have behaved as if it had a natural frequency of five times its normal value. On attempting to obtain a resonance curve, however, it was found that several complications were introduced which prevented the full compensation aimed at from being realized, although sufficient evidence was obtained from the results to support the truth of the theory. In all cases the complications were traced to the valve system, and not to the link. Firstly, the valve system, owing to leakage to earth from the grid *viâ* the cap of the valve etc., was not perfectly electrostatic; and, secondly, it was found practically impossible, when the system was compensated, to ensure that the valve was always operated only on the straight part of the characteristic curve between the lower bend and zero. It will be observed (fig. 9) that, when the system was compensated, the grid of the valve was connected to a point between the two condensers, so that it was insulated from earth on the positive side of the grid battery GB. Consequently the latter, owing to the leakage to earth from the grid side of the battery (which, of course, tended to maintain the grid at zero potential), could not keep the grid at the required mean potential of -12 volts. When an alternating potential was applied to the ends of the link, a fraction of it was passed on to the grid. Suppose that the first half-cycle was in the positive direction. This tended to raise the potential of the grid above its previous value of zero, thus giving rise to a grid current. This current prevented the grid from becoming charged to as high a positive potential as would have been the case had there been no grid current.

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In the negative half-cycle the grid current was zero, so that the grid became charged to its full negative value. The mean potential of the grid over the cycle was therefore slightly negative. During succeeding cycles the mean value gradually became more negative until it attained a steady value, at which value it remained as long as the oscillations were maintained. When, however, these ceased, the leakage caused the grid potential to rise to zero once more. This phenomenon is a well-known one, and is made use of in every modern wireless receiver employing a valve detector. In the above system, condenser C functioned as the "grid condenser," and the leakage across the valve cap as the "grid leak." It should be observed that the grid current only flowed while the potential of the grid was actually changing. When the latter was steady the grid current was zero.

An oscillogram illustrating this phenomenon was obtained by photographing the curve traced by the spot at the moment when an alternator (frequency 780·0) was suddenly connected to the link. This curve is shown in fig. 11 (Pl. I.). In this case the change in the mean value of the grid potential was sufficient to carry the working range beyond the bend in the characteristic curve. The mean value of the plate current before connexion was 8·1 milliamps, and after connexion 1·4. On reference to fig. 5 it will be observed that this new value was in the region of the lower bend. If fig. 11 be examined it will be observed that the first few oscillations were recorded with a greater amplitude than those recorded when the grid had taken up its new mean potential. This was accounted for by the movement of the operating range on to the curved portion of the valve characteristic curve, so that a given change of grid potential produced a smaller change in the plate current than when operating on the steep straight portion. This effect will be referred to later. The presence of the small oscillation on the left may be explained by the fact that when the system was compensated the grid was not connected to earth, but to a point between the two condensers which served as a "floating neutral." Any slight capacity effect between condenser C_1 and the alternator, or leakage across the switch terminals, thus altered the potential of this neutral and also of the grid. Theoretically there should have been no oscillation recorded in this section of the curve.

The resonance curve (fig. 8 (*b*)) was obtained in a similar manner to the method employed when the instrument was uncompensated (*i. e.* measuring the amplitude of oscillation

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for voltages at various frequencies). In this case, however, greater care had to be taken owing to the complications involved. Before taking each reading it was necessary to observe whether the mean value of the plate current had fallen below the value corresponding to -12 volts (viz. 5·16 milliamps), and, if so, to raise it slightly by diminishing the voltage applied to the link. In some cases, however, especially at frequencies above about 300, it was impossible to obtain satisfactory readings if the applied voltage was too low, so that the mean value of the plate current fell below the value corresponding to -12 volts. In these cases, as was expected, the amplitude scale was much less than its theoretical value.

It should be observed that, with this arrangement, it was impossible to obtain the amplitude for a steady deflexion in the manner employed for the uncompensated instrument (viz., by applying a steady potential to the link) owing to the grid current rendering the positive value equal to zero. Accordingly, its theoretical value was calculated from the values of the condensers C and C_1, and the steady deflexion obtained when uncompensated. The value so obtained was used for reducing the readings at other frequencies to the same scale as for the uncompensated curve.

The compensated curve is shown in fig. 8 (*b*) drawn so as to have the same theoretical zero amplitude scale as curve (*a*). The dotted curve (*c*) is the curve that should have been obtained in this case if the compensation had been perfect. It will be observed that curve (*b*) is flat for a range extending from a frequency of about 60 to about 200. Over this range, then, the compensation is perfect. Any compound oscillation composed of frequencies between 60 and 200 would therefore be correctly recorded by the instrument. If curve (*a*) be examined it will be observed that the amplitude scale varies considerably over this range (viz., from 84 to 61). Nearer the zero, however, curve (*b*) dips down. This is due to two causes, both of which are peculiar to this apparatus. (1) The damping in the instrument, as has already been explained, is not constant. For low frequencies, it is found that the damping is very much greater than for high ones—a fault no doubt due to the method employed for applying the damping. When the system was compensated, R was calculated from the value of the damping factor at the centre of the desired range. Hence, at low frequencies, R was less than the value necessary to ensure full compensation, so that the system was under-compensated. (2) The combined effect of "grid condenser rectification"

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and the leakage to earth is much more marked at low frequencies than at high ones, owing to the fact that the time between two cycles (during which leakage tends to restore the grid to zero potential) is greater. This results in the oscillations of the grid potential not reaching their full value. Hence, the variation in plate current is less than it should have been. Both these effects would tend to lower the amplitude scale, and so help to explain the dip near zero.

Above a frequency of about 200, curve (*b*) falls as the frequency increases. This is due, as has already been explained, to the change in the mean value of the grid potential being sufficiently great to move the working range to the bend of the characteristic curve.

The curve shown in fig. 8 (*b*) is a typical one. In all cases, the dip near zero and the fall in amplitude at high frequencies were observed. If the damping of the instrument had been uniform, no doubt the compensated curve would have approximated much better to curve (*c*) than it does. In any case, if curve (*b*) be compared with curve (*a*), fig. 3, which is the best obtainable in any uncompensated instrument, it will be observed that it is a great improvement even on this, and the improvement on curve (*a*) fig. 8, the best obtainable with this particular instrument, is very marked. The range over which a 4 per cent. error is incurred in curve (*b*) is from 47 to 250, which, taking the natural frequency as 725·0, is 0·28*n*. In curve (*a*) fig. 8, the range for this error is from 0 to 14·5, or 0·02 *n*, while in curve (*a*) fig. 3, the best obtainable uncompensated curve, the extent of the range is only 0·2 *n*.

To illustrate the effect of compensation on the appearance of oscillograms, the curves shown in figs. 12 and 13 (Pl. I.), were taken. Two alternators were connected in series, and arranged so as to give approximately the same R.M.S. voltage. One gave a frequency of 52 per second, and the other about 250. The resulting "mixture" of alternating E.M.F.s was then analysed by the instrument, firstly compensated, and secondly, uncompensated. No change was made in the circuits or alternators etc. during the experiment except to introduce the compensating link. As the whole time of the experiment was only about six minutes, the machines can be assumed to have been running steadily. Fig. 12 (Pl. I.) shows the curve as recorded by the uncompensated instrument, and fig. 13, by the compensated system. In the latter curve, it will be observed that the amplitudes of the two components are much more nearly

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equal than in the former, thus showing the great advantage obtained by compensating the system.

These curves have no particular significance beyond illustrating "compensation." The two frequencies (viz., 52 and 250) were employed so as to be at the extreme ends of the compensated range. As one is about five times the other, the curve appears as if it were composed of a fundamental frequency of 52 with a superimposed fifth harmonic of about the same amplitude. The relative phases of the two components are not constant owing to the fact that one frequency is not an exact multiple of the other. While the curves serve as an excellent example of amplitude compensation, for obvious reasons they give no indication of any phase compensation. It is found, however, that the phase lag is compensated in a similar manner to the amplitude. By photographing the oscillogram of an inductor alternator having a frequency of 100, and a pronounced third harmonic, it was found that the relative phases of the fundamental and the harmonic were very different in the two curves.

From the above, it is clear that, in spite of the difficulties of working with this apparatus, an oscillograph can be compensated for amplitude and phase, and that its usefulness is thereby increased. The low frequencies employed in the experiments, it should be observed, were only a matter of convenience for testing the theory, as the compensation should apply equally well to instruments having higher frequencies of vibration. The valve, which was necessary with this type of oscillograph, also introduced several difficulties that prevented the desired results from being fully realized. From the results obtained, however, the conclusion can fairly be drawn that if a perfectly electrostatic oscillograph of small capacity, large sensitiveness, and uniform damping could be obtained, it would be possible considerably to increase its working range by this method of compensation. Apparently the only source of trouble in the experiments was the valve portion of the apparatus. The link gave rise to none.

The experiments are interesting from another point of view. The oscillograph consisted of a telephone receiver, and the frequencies employed lay within the range of human audibility. For perfect reproduction of sound the amplitude of vibration of the diaphragm should be independent of the frequency of vibration, so as to produce sounds of intensities proportional only to the current passing through the coils of the magnet. Possibly, therefore, compensation of the kind

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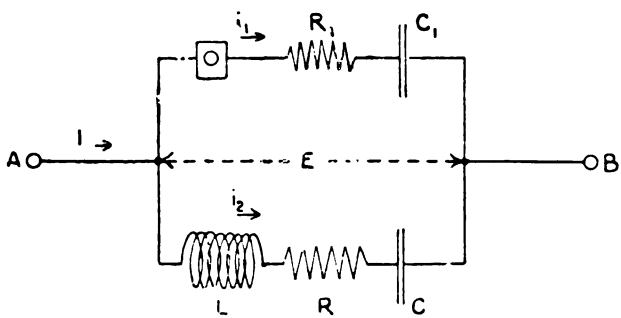
contemplated here might be applied with advantage to ordinary telephone receivers and loud speakers to improve the reproduction of the sound. No experimental work, however, was undertaken in this direction, this being put forward simply as a suggestion.

Application to Current Oscillographs.

So far, potential oscillographs only have been dealt with. It may be shown theoretically, however, that a current oscillograph can also be compensated, although such an instrument could only be used if the impedance of the circuit in which it is inserted were large compared with the impedance of the system including the oscillograph and the compensating link.

In this case, as only a fraction of the current is to be supplied to the oscillograph, the link will have to be some form of a shunt. By an analysis similar to the one used in the case of the potential oscillograph, it may be shown that the required circuit is as shown in fig. 10. The terminals A

Fig. 10.



and B, instead of being connected to the oscillograph, are connected by two circuits in parallel—one containing the oscillograph O, the resistance R_1, and the condenser C_1, and the other an inductance L, a resistance R, and a condenser C. The current oscillograph is supposed to have no appreciable inductance or resistance, and to conform to the equation

$$(D^2 + kD + n^2).x = Ai,$$

where A is a constant, and i the current flowing through the instrument. Denoting the main current by I, the branch

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currents by i_1 and i_2, and the back E.M.F. due to the impedance of the system by E, we get:

$$\left(R_1+\frac{1}{C_1D}\right)i_1=\left(LD+R+\frac{1}{CD}\right)i_2=E,$$

or

$$i_2=\frac{\left(R_1D+\frac{1}{C_1}\right)}{\left(LD^2+RD+\frac{1}{C}\right)}i_1.$$

Now,

$$I=i_1+i_2=\frac{\left[LD^2+(R+R_1)D+\left(\frac{1}{C}+\frac{1}{C_1}\right)\right]}{\left(LD^2+RD+\frac{1}{C}\right)}i_1,$$

whence

$$i_1=\frac{\left(LD^2+RD+\frac{1}{C}\right)}{\left[LD^2+(R+R_1)+\left(\frac{1}{C}+\frac{1}{C_1}\right)\right]}I.$$

Since

$$x=\frac{Ai_1}{(D^2+kD+n^2)},$$

we get

$$x=\frac{\left(LD^2+RD+\frac{1}{C}\right)}{\left[LD^2+(R+R_1)D+\left(\frac{1}{C}+\frac{1}{C_1}\right)\right]}\times\frac{AI}{(D^2+kD+n^2)}.$$

As before, making $\frac{1}{LC}=n^2$, and $\frac{R}{L}=k$, and denoting $\frac{1}{LC_1}$ by n_1^2, and $\frac{R_1}{L}$ by k_1, we get

$$x=\frac{(D^2+kD+n^2)}{[D^2+(k+k_1)D+(n^2+n_1^2)]}\times\frac{AI}{(D^2+kD+n^2)}$$

$$=\frac{AI}{[D^2+(k+k_1)D+(n^2+n_1^2)]}.$$

The form of this expression is the same as that obtained in the case of a potential oscillograph. The main current I

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would therefore be recorded by the oscillograph O in the same way as if the terminals A and B had been connected to an oscillograph having a periodicity of $\sqrt{n^2+n_1^2}$, and damping factor $k+k_1$, so that the oscillograph would be compensated in a similar manner to the potential oscillograph. A difficulty arises, however, in the practical application of this, for it has been assumed that the oscillograph O has no appreciable resistance or inductance. While this is usually so for the oscillograph itself, in the compensated system which replaces the oscillograph the impedance is not negligible.

Conclusion.

The application of this method of increasing the working range of an oscillograph is not confined to electrical instruments, as no assumption as to the nature of the applied force was made in the theory. It should be equally adaptable to any variety of oscillograph (*e. g.*, one used for recording sound waves, etc.), provided that a suitable type of link can be found. The type of link naturally depends upon the function of the particular instrument, and its composition and constants would have to be determined in each case by a mathematical analysis similar to the one shown for the potential oscillograph. It is hoped, however, that the two cases dealt with (*i. e.*, potential and current oscillographs) and the account of the experimental test carried out in the one case, will serve as an interesting introduction to a method for increasing the usefulness of oscillographs, and similar instruments, the operation of which depends upon forced oscillations.

The experimental work in connexion with the above was carried out in the physical laboratories of the University College of North Wales, Bangor, and the writer desires to express his obligation to Dr. Taylor Jones for the interest taken by him in the work, and for suggestions and advice in carrying it out.

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II. *The Effect of a Magnetic Field on the Electrical Resistance of Liquid Metals and Alloys.* By E. J. WILLIAMS, *M.Sc. (Wales), lately University Research Student, University College of Swansea* *.

THE work that has been done on the effect of a magnetic field on the electrical resistance of liquid metals and alloys is briefly reviewed by L. L. Campbell †, and the following is a quotation from the section concerned :—

"Drude and Nernst ‡ (1891) observed that the resistance of mercury in a field of 8000 gauss increased about ·2 per cent., whilst that of molten bismuth at 290° C. increased by ·4 per cent. The same year Des Coudres § called attention to the fact that the apparent increase might be attributed to heating of the metal by the current. The work of Berndt ‖ (1907) seemed to confirm the contention of Des Coudres. He found that the smaller the tube the less the increase of resistance. In fields from 1000 to 3000 gauss the increase of resistance was not more than ·00004 per cent. for mercury and ·004 per cent. for molten bismuth. Rossi ¶ (1911) measured the resistance of mercury and of mercury-bismuth amalgams in tubes of from ·5 mm. to ·7 mm. diameter, in fields from 3350 to 4450 gauss. In both mercury and the amalgam the change of resistance was found to increase with the field, the diameter of the tube, and the concentration of the amalgam. The above subject would seem to deserve further investigation."

Besides the investigations mentioned here, an extensive series of experiments has been carried out by T. J. Jones ** and they are described elsewhere.

Drude and Nernst, and Berndt regarded the effects observed as being due to "electrodynamic" action, and they maintained that there was no true resistance change in liquid metals. Des Coudres regarded the effect as being probably due to heating of the metal by the electric current. On the other hand, Patterson †† (1902) seemed to regard it as a true effect, since he applied to his experimental results a formula developed by Sir J. J. Thomson for a true effect.

* Communicated by Prof. E. J. Evans, D.Sc., Univ. Coll. of Swansea.
† 'Galvanomagnetic and Thermoelectric Effects' (1923).
‡ Drude & Nernst, Wied. *Ann.* xlii. (1891).
§ Des Coudres, *Verh. D. Phys.* xxiii. (1907).
‖ G. Berndt. *Ann. d. Phys.* xxiii. (1907).
¶ R. Rossi, *Nuov. Cim.* (6) ii. (1911).
** T. J. Jones, *infrà*, p. 46.
†† Patterson, Phil. Mag. iii. p. 643 (1902).

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Recently W. M. Nielson * (1924), who applied a great pressure to the mercury contained in a fine capillary tube in order to eliminate spurious effects caused by mechanical motion of the mercury, has shown that $\frac{\delta r}{r}$ for a field of 16,000 gauss is less than ·0003 per cent. The upper limits to $\frac{\delta r}{r}$ for mercury found by Berndt and Nielson do not, however, warrant the general conclusion that metals and alloys in the liquid state exhibit no true magneto-resistance effect. In the first place, these upper limits to the effect in mercury are not appreciably smaller than the actual effect observed in certain solid metals, such as platinum. Moreover, the galvanomagnetic effects for *solid* mercury are abnormally small in comparison with those exhibited by other metals. Fenninger † has found, for instance, that the Hall coefficient for solid mercury is less than ·00001, which limit is four times smaller than the Hall coefficient for tin (which, of all other metals, possesses the smallest coefficient), and twenty times smaller than the Hall coefficient for platinum ‡.

It is proposed in this paper, first, to discuss theoretically the effect of a magnetic field upon the resistance of liquid conductors, and then to examine the experimental results in the light of the theory developed. It will be shown that there is evidence for the existence of a true resistance change in certain liquid metals and alloys, and moreover it will be found that the "spurious" effect is itself of considerable interest.

Theoretical Discussion.

It is assumed that the change of resistance of a column of liquid metal, due to the action of a magnetic field, can only arise from the following two effects :—

(1) A change of resistivity of the metal.

(2) A change of resistance consequent upon the expenditure of energy required to maintain hydrodynamic currents set up in the liquid by the action of the magnetic field upon the electric current.

* Nielson, Phys. Rev. p. 302 (Feb. 1924).

† Fenninger, Phil. Mag. xxvii. pp. 109–112 (Jan. 1914).

‡ The values taken for tin and platinum are those at room temperatures, but as the Hall coefficient decreases with temperature this only strengthens the argument.

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The first takes account of a possible true effect, and the increase of resistance, $\delta_1 r$, due to it bears to the original resistance r a ratio which is independent of the size and shape of the column. It can, therefore, be represented by Ar, where A is independent of the dimensions of the column.

The second effect will now be considered in detail. In the first place it can be shown that, under the action of the magnetic field, the liquid metal will in general not remain in equilibrium. Let α, β, γ be the components of the magnetic field H, and I_x, I_y, I_z the components of the electric current I, at a point x, y, z in the liquid. Then from Ampère's law the force, P, per unit volume acting upon the liquid at x, y, z has the components $X=\gamma I_y-\beta I_z$, $Y=\alpha I_z-\gamma I_x$, $Z=\beta I_x-\alpha I_y$. If the liquid is to remain at rest, the force P must be derivable from a single-valued potential-function. That will be the case provided the following relations hold at all points in the liquid:

$$\frac{\partial X}{\partial y}-\frac{\partial Y}{\partial x}=0,\quad \frac{\partial Y}{\partial z}-\frac{\partial Z}{\partial y}=0,\quad \frac{\partial Z}{\partial x}-\frac{\partial X}{\partial z}=0. \quad . \quad (1)$$

Since the magnetic field and electric current are quite independent, these relations will in general not be satisfied, and the liquid will consequently be set in motion.

In this connexion it should be mentioned that it is possible to have cases in which the equilibrium conditions are satisfied. The simplest and most practical case is that in which the magnetic field and electric current are constant in magnitude and direction throughout the liquid (when $\frac{\partial}{\partial x}=\frac{\partial}{\partial y}=\frac{\partial}{\partial z}=0$). An experiment under these conditions was carried out by T. Jones* in his investigation of the effect of the shape and position of the current leads, and his observations are in accordance with these calculations. He found that as the leads were pushed nearer together from a position in which the mercury, contained between them in a cylindrical glass tube, extended outside the magnetic field, to a position in which the mercury was entirely in a uniform field, the resistance change decreased to a hundredth of its first value. The leads did not completely fill the tube so that the electric current was not absolutely uniform, and this probably accounted for the small change still present in the second position. Jones used tubes of diameter of the order of

* *Loc. cit.*

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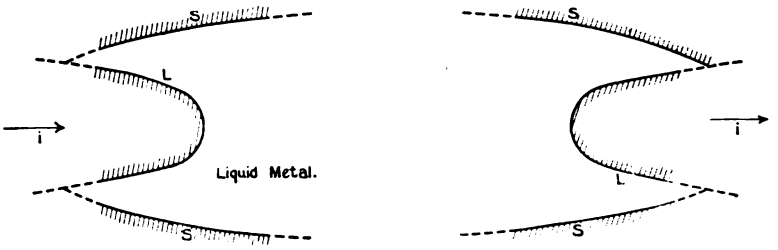
·5 cm., and in such cases, as we shall see later, the real effect $\delta_1 r$ is negligible.

In discussing the increase of resistance due to the motion of the liquid, it is necessary to consider a general case since the experiments which have been carried out are not confined to straight cylindrical columns. In some cases bent tubes have been used, and in others leads extending into the liquid in the field, and not filling the tube.

Let the electric current enter the liquid metal from the surfaces L, the liquid being bounded elsewhere by the insulating surfaces S, there being no free surface of the liquid * (see fig. 1).

Fig. 1.



Let i be the total current traversing the liquid, I be the resultant current per unit area at the point x, y, z, and H be the resultant field at x, y, z. The force acting upon the liquid per unit volume at the point x, y, z is then equal to the vector product of H and I (VHI). There is no need to take into account the forces acting upon the liquid initially and under the action of which the liquid was in equilibrium, as it can be shown that they have no effect upon the motion produced. Let p be the increase of pressure at (x, y, z) at time t after the application of the field and current. Then the differential equations of motion of the liquid are :

$$\rho\frac{du}{dt} = X - \frac{\partial p}{\partial x} + \eta\left(\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2}\right),$$

with similar equations for $\rho\frac{dv}{dt}$ and $\rho\frac{dw}{dt}$, and

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} = 0, \quad . \quad . \quad . \text{ equations (2)}$$

* This is satisfied to all intents and purposes in all actual cases, any free surface, which there may be, being far from the affected portion of the liquid.

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u, v, w being the components of velocity of the liquid at (x, y, z), ρ the density of the liquid, and η its viscosity. These equations, together with the boundary conditions, determine the motion produced. The motion will not necessarily reach an absolutely steady state, in which the velocity at a point is the same at all instants. Such a state is not reached in the case of a liquid in turbulent motion. The motion will, however, reach a state in which the velocity at any point, when averaged over a sufficiently large interval of time, is independent of the time. If this velocity be denoted by $\bar{u}$, then the mean work done by the force "HI" per unit volume, per unit time, at (x, y, z) will be equal to the component of $\bar{u}$ parallel to $\mathrm{VHI} \times \mathrm{VHI}$, *i. e.* $\mathrm{S}\bar{u}\mathrm{VHI}$, S denoting scalar product. The mean total work done per unit time is therefore $\iiint_\Sigma \mathrm{S}\bar{u}\mathrm{VHI}\,d\Sigma$, where Σ represents the space occupied by the liquid. This is equal to the mean rate of dissipation of energy due to the motion, and if we denote it by F, and the corresponding increase of resistance by $\delta_2 r$, we evidently have

$$i^2 . \delta_2 r = \mathrm{F} = \iiint_\Sigma \mathrm{S}\bar{u}\mathrm{VHI}\,d\Sigma,$$

$$\text{or} \qquad \delta_2 r = \frac{\mathrm{F}}{i^2} = \frac{1}{i^2}\iiint_\Sigma \mathrm{S}u\mathrm{VHI}\,d\Sigma. \quad . \quad . \quad . \quad . \quad (3)$$

In order to obtain the exact value of F *, it is necessary in the first place to determine $\bar{u}$—*i. e.*, to solve equations (2). This would be most difficult, and probably impossible. However, much information can be obtained concerning F by means of the method of dimensions. As we have seen, $\mathrm{F} = \iiint_\Sigma \mathrm{S}u\mathrm{VHI}\,d\Sigma$, so that it depends only upon those quantities which affect $\bar{u}$, HI, and Σ. The quantities which can affect $\bar{u}$ are the independent variables, other than time (of which $\bar{u}$, by its definition, is independent), contained in the differential equations (2), and the corresponding boundary conditions. It follows that F can depend only on HI, η, ρ, and Σ.

In most experiments concerned with this problem, the magnetic field is constant over a certain area and then falls off comparatively quickly. No use will be made of this fact here, but it will be assumed that the values of H at

* It has been found as a result of approximate calculations in certain cases (E. J. Williams, Thesis for M.Sc., Wales, 1924) that the increase of resistance, consequent upon the effect under consideration, is of the same order as that of the increase actually observed in those cases.

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any two points always bear the same ratio to one another *. The maximum value, denoted by h, will be taken as the standard value. Then the value of H at any point can be expressed in the form $h\times$ (function of coordinates of the point and geometry of the field).

When the liquid is in motion in the magnetic field, induced e.m.f.s are set up. These will produce extra electric currents, which will be superimposed upon the primary current. These induced currents are, however, probably negligible compared with the primary current; for they bear to the latter a ratio which is of the same order as the ratio of the induced back e.m.f. to the primary forward e.m.f., which is in turn equal to the ratio of the increase of resistance, $\delta_2 r$, to the initial resistance r. The latter ratio is generally much less than ·01, and it therefore follows that the induced currents are very small compared with the original current, and they will be neglected.

The distribution of the current is then governed by the differential equations $\operatorname{div} \mathrm{I}=0$, $\operatorname{rot} \mathrm{I}=0$, and the boundary conditions, which involve the total current i traversing the liquid, the ratio σ/σ' of the resistivity of the liquid to that of the leads, and the geometry of the boundary. It follows that I can be expressed in the form:

$$\mathrm{I} = i \times (\text{function of } \sigma/\sigma') \times (\text{function of } x, y, z \text{ and geometry of boundary}),$$

and the product HI in the form:

$$\mathrm{HI} = hi \times (\text{function of } \sigma/\sigma') \times (\text{function of } x, y, z, \text{ geometry of boundary and geometry of magnetic field}).$$

h and i therefore always appear together as the product "hi." The dimensions of "hi" are those of $\frac{\text{Force}}{\text{Length}}$, *i. e.* MT^{-2}. The dimensions of the viscosity, η, are $\mathrm{ML}^{-1}\mathrm{T}^{-1}$, of the density, ρ, ML^{-3}, whilst $\frac{\sigma}{\sigma'}$ is of no dimensions. Geometrically similar systems are considered;

* The magnetic field is generally furnished by an electromagnet with an iron core. The assumption made would be absolutely correct if the permeability μ of the iron did not vary with the magnetizing force. The permeability μ measures the refractive index of the lines of force at the surface of the iron, and as it is always very large (of the order of 1000) the lines leave the surface almost normally, and the possible variation in μ alters but little the angle which the lines make with the surface on emergence. As a result, the geometry of the field outside remains practically constant.

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the similarity applying to the variation of the magnetic field as well as the boundary of the liquid. The dependency upon the configuration of the system is thus nominally reduced to dependency upon its scale, which will be denoted by "s," and is of the dimensions of length. The dimensions of F are those of $\frac{\text{Energy}}{\text{Time}}$, *i.e.* ML^2T^{-3}; and the expression for F, which can only involve hi, η, ρ, s, and $\frac{\sigma}{\sigma'}$, must be of these dimensions also *. A general expression satisfying this dimensional relation is

$$F = B \cdot \frac{h^2 i^2 s}{\eta} \cdot f\left(\frac{\eta^2}{hi\,s\rho}\right) \cdot \phi\left(\frac{\sigma}{\sigma'}\right),$$

where F and ϕ are any functions whatever, and B a numerical constant. Therefore, from equation (3)

$$\delta_2 r = B \cdot \frac{h^2 s}{\eta} \cdot f\left(\frac{\eta^2}{hi\,s\rho}\right) \cdot \phi\left(\frac{\sigma}{\sigma'}\right), \quad . \quad . \quad . \quad . \quad (4)$$

and the total increase of resistance is given by

$$\delta r = \delta_1 r + \delta_2 r = A \cdot r + B \frac{h^2 s}{\eta} \cdot f\left(\frac{\eta^2}{hi\,s\rho}\right) \cdot \phi\left(\frac{\sigma}{\sigma'}\right). \quad . \quad (5)$$

The application of (5) to particular cases will now be considered.

Case in which the motion of the liquid is steady.

The motion of a liquid is said to be steady when the velocity at any point is the same at all instants. The viscosity of a liquid tends to bring about steady motion, whilst the momentum of the motion has the opposite effect. For these reasons, small linear dimensions and small velocities are favourable to steady motion. The experiments which are pre-eminently included in the case of steady motion are, therefore, those in which the magnetic field, the electric current traversing the liquid, and the dimensions of the column of liquid, are small.

The differential equations governing the steady motion of a liquid are obtained from (2) by putting $\frac{du}{dt} = \frac{dv}{dt} = \frac{dw}{dt} = 0$. It can then be shown that the velocity at any point is

* The dimensions attributed to the various quantities are those which they possess in the differential equations.

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proportional to "hi," and is always in the same direction. It follows that

$$S\bar{u}VHI \propto h^2 i^3,$$

$$\therefore \quad \delta_2 r \propto \frac{F}{i^2} \propto \frac{h^2 i^3}{i^2} \propto h^2.$$

But from (4),

$$\delta_2 r = B \cdot \frac{h^2 s}{\eta} \cdot f\left(\frac{\eta^2}{hi s\rho}\right) \cdot \phi\left(\frac{\sigma}{\sigma'}\right)$$

$$\therefore \quad f\left(\frac{\eta^2}{hi s\rho}\right) = \text{constant},$$

so that

$$\delta_2 r = B \cdot \frac{h^2 s}{\eta} \cdot \phi\left(\frac{\sigma}{\sigma'}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

and

$$\delta r = \delta_1 r + \delta_2 r = Ar + B \cdot \frac{h^2 s}{\eta} \cdot \phi\left(\frac{\sigma}{\sigma'}\right). \quad (6\,a)$$

Berndt *, using a capillary tube of diameter 0·29 mm., containing liquid mercury, failed to observe a change of resistance on the application of a field of 3000 gauss, and from the degree of accuracy attainable in his experiments, concluded that the change, if present, was less than ·00004 per cent. This result sets an upper limit to $A = 4 \times 10^{-7}$, for a field of 3000 gauss, the second term in (6 *a*) being essentially positive. Incidentally, with a tube of diameter 0·37 mm., Berndt observed a change of $50 \times 10^{-7} r$, *i. e.* more than 12 times the change in the tube of diameter 0·29 mm. This increase in $\frac{\delta r}{r}$ is attributed to the second term in (6 *a*), *i. e.* to the hydrodynamic effect. The large increase in $\delta_2 r$ was probably due not only to the difference in the diameters of the tubes, but chiefly to the conditions obtaining with the tube of 0·29 mm. diameter being nearer the equilibrium conditions.

W. M. Nielson † (1924) has shown that $\frac{\delta r}{r}$ for mercury for a field of 16,000 gauss is less than 3×10^{-6}, which corresponds to an upper limit to $A = 1 \times 10^{-7}$, for a field of 3000 gauss ‡.

Reference might here be made to the methods adopted in order to eliminate or rather to minimize the spurious effect. In the theory presented here, the spurious effect is represented by $\delta_2 r$. It is seen to be directly proportional to the

* *Loc. cit.* † *Loc. cit.*

‡ In making this reduction, it is assumed that the true resistance increase is proportional to (field)^2.

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linear dimensions of the system (equation 6), which is in accordance with the result obtained by various observers, that the spurious effect can be diminished by using tubes of finer bore. In addition, however, to using a fine bore tube, Nielson applied a pressure of about 10 atmospheres to the mercury. The effect of such a pressure on the viscosity is small, so that the diminution of $\delta_2 r$ effected by this means was inappreciable. The ideal method seems to be one which ensures that the current and field are uniform throughout the liquid, when, as already shown, the liquid will not be set in motion and therefore $\delta_2 r = 0$.

Having obtained from the experiments of Berndt and Nielson an upper limit to A, we shall consider the results obtained by Rossi *, who used fields of from 3350 to 4450 gauss. With a field of 3350 gauss he observed an increase of resistance of $37 \times 10^{-7} r$, in a capillary tube of diameter 0·7 mm. containing mercury. The value of A for this field (from Nielson's results) is less than 1×10^{-7}, so that at least 97 per cent. of the increase observed by Rossi with pure mercury was due to motion of the mercury, and is represented by $\delta_2 r$.

In the case of steady motion the expression for $\delta_2 r$ is independent of the current "i" (equation 6). Rossi does not mention any dependence of δr upon the current traversing the mercury, and consequently we may assume that the motion in his experiments was steady and equation (6) ought therefore to apply. According to this equation δr is proportional to the square of the field, and an analysis of Rossi's results as given in Table I. shows that this is the case.

TABLE I.

Magnetic Field.	Tube of diameter = 0·7 mm.		Tube of diameter = 0·5 mm.	
	$\delta r \times 10^7$, in ohms.	$\frac{\delta r}{h^2} \times 10^{14}$.	$\delta r \times 10^7$.	$\frac{\delta r}{h^2} \times 10^{14}$.
3350	69	61	57	51
3640	78	59	66	50
3930	92	60	77	50
4190	104	59	86	49
4450	123	62	104	52

* *Loc. cit.*

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Rossi also investigated the effect of a magnetic field upon the resistance of liquid bismuth amalgams. If no true effect was present in these cases also, the values of δr for the amalgams would also be given by *

$$\delta r = \delta_2 r = \mathrm{B}\frac{h^2 s}{\eta}$$

This equation applies to geometrically similar systems, and in all probability holds in the case of all experiments carried out with the same tube. The experimental results obtained with a capillary tube of diameter 0·5 mm. are given in Table II. The values of δr calculated on the assumption that it entirely consists of the hydrodynamic effect are also given †. In making the calculations, the viscosity of dilute bismuth amalgams is taken to increase at the rate of 1 per cent. for the addition of 1 per cent. of bismuth by weight to the mercury ‡.

It is seen from this table that there is a more or less consistent increase of δr with the concentration of bismuth. In fact, the mean percentage increases due to the addition of ·5 per cent. and 1 per cent. are 10 and 19 respectively, whilst for the saturated bismuth amalgam the increase in δr is 66 per cent. The calculated increase of resistance, $\delta_2 r$, due to the motion of the liquid, however, decreases upon the addition of bismuth, and in order to account for the experimental results it is necessary to assume the existence of a true resistance change in bismuth amalgams. The magnitude of this true effect is given by

$$\delta_1 r = \delta r - \delta_2 r,$$

and its values for the various concentrations and fields are given in Table II. The irregular variation of $\delta_1 r$ with the field is probably due to experimental error. Since $\delta_1 r$ represents a true effect, $\frac{\delta_1 r}{r}$ should be independent of the shape and dimensions of the column of amalgam experimented upon, so that its value for the 0·7 mm. tube should be the same as that for the 0·5 mm. tube. Rossi only used a saturated bismuth amalgam, in addition to mercury, in the 0·7 mm. tube, and a comparison of the results for this

* In Rossi's experiments the leads are sufficiently far removed from the field so as not to introduce any complications, and consequently the term $\phi\left(\frac{\sigma}{\sigma'}\right)$ is a constant and can be included in B.

† The constant B is calculated from the value of δr for pure mercury.

‡ This is the result of an approximate determination by the writer.

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TABLE II.

Magnetic Field. (gauss).	Increase of Resistance, δr.									
	Pure Mercury (observed).	Amalgam containing ·5 % Bi.			Amalgam containing 1 % Bi.			Amalgam saturated at 12° C.		
		δr (obs.).	$\delta_2 r$ (calc.).	$\delta r - \delta_2 r = \delta_1 r$.	δr (obs.).	$\delta_2 r$ (calc.).	$\delta r - \delta_2 r = \delta_1 r$.	δr (obs.).	$\delta_2 r$ (calc.).	$\delta r - \delta_2 r = \delta_1 r$.
3350	57	61	57	4	70	56	14	81	56	25
3640	66	75	66	9	83	65	18	115	64	51
3930	77	86	77	9	95	76	19	133	75	57
4190	86	91	86	5	102	85	17	156	84	72
4450	104	116	103	13	118	103	15	169	101	68

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amalgam shows that the mean value of $\frac{\delta_1 r}{r}$ is 32×10^{-7} for the 0·7 mm. tube and $32\frac{1}{2} \times 10^{-7}$ for the 0·5 mm. tube. However, we must not lay too much stress on this experiment, because there is some irregularity amongst the separate values.

If the percentage of bismuth is denoted by p, the mean value of $\frac{\delta_1 r}{r} \cdot \frac{1}{p}$ due to a field of about 4000 gauss is $1{\cdot}0 \times 10^{-6}$, and this can be taken to be the estimated true resistance change in bismuth amalgams. It is of the same order as that observed in solid metals.

The results obtained for a saturated bismuth amalgam at 190° C. seem to indicate that the true effect is much less at this temperature than at room-temperature. This decrease with temperature is also a general characteristic of the true resistance changes observed in solids. Exact calculations cannot be made owing to the lack of data concerning the viscosity of saturated bismuth amalgams at this temperature.

There is also a certain amount of evidence of a true resistance change in the work of Berndt. Since he used tubes of smaller diameter than those used by Rossi, it can be assumed that the motion was steady in his experiments, and therefore that equation ($6a$) is applicable to his results. It was found that the measure of resistance, δr, in molten bismuth decreased from 1/230 per cent. to 1/400 per cent. on heating the metal from 420° C. to 500° C. The viscosity decreases with the temperature, so that $\delta_2 r$ increases on heating from 420° to 500°. It therefore follows that the bulk of the 1/230 per cent. increase observed at 420° C. is a true effect, which decreases with the temperature.

The existence or non-existence of a true magneto-resistance effect of magnitude comparable with that observed in solids in the case of liquids is of importance to the theory of electrical conductivity. According to some theories the effect should not be exhibited by liquid metals, as they are non-crystalline *. Thus should the evidence, which has been presented here, for the existence of a true effect in bismuth amalgams and molten bismuth be substantiated, these theories would probably have to be abandoned or at any rate considerably modified.

* From evidence provided by work on the vapour pressures and conductivities of amalgams, the added metal in all probability exists in the monatomic state, and therefore an essentially non-crystalline state.

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Case in which the motion of the liquid is not steady.

Drude and Nernst* (1891) and independently Jones† (1924) found that, in their experiments, the increase of resistance δr was dependent upon the current "i" traversing the liquid. The order of magnitude of δr in these cases is such that the increase is entirely to be ascribed to the hydrodynamic effect, which is represented by $\delta_2 r$. Now in the general expression for $\delta_2 r$, given in equation (4), i only appears in the term $f\left(\frac{\eta^2}{hi\,s\rho}\right)$. It was found in discussing the first case that if the motion is steady $f\left(\frac{\eta^2}{hi\,s\rho}\right)$ is constant. The dependency of $\delta_2 r$ upon the current must therefore be attributed to the production of turbulent motion in the liquid. This supposition, and its various other theoretical consequences, will now be considered.

It is well known that, even in the case of rectilinear motion of liquids, the motion becomes turbulent, if the velocity or other quantities concerned reach certain critical values. The type of motion with which we are concerned here is that of a liquid in an enclosed space, and is of necessity "curvilinear." The curvature of the stream-lines makes the motion much more susceptible to turbulence than rectilinear motion. In support of this statement, the results of certain experiments due to Gibson and Grindley ‡ may be mentioned. They found that the value of $\frac{v_c d}{\nu}$, where v_c is the critical velocity, and d and ν the diameter of the pipe and kinematic viscosity of the liquid respectively, in the case of motion through a pipe of diameter ·32 cm., wound round a drum of diameter 36 cm., was 130. The value of the same quantity in the case of motion through a straight pipe is about 2000. The average curvature of 18 cm. radius imposed upon the motion in consequence of the curvature of the pipe, therefore, increases the tendency, for turbulence about 15 times. The radius of curvature of the stream-lines, in the motion under consideration here, is of the order of a millimetre. It is impossible to make exact calculations of the velocity, etc.; but as the result of an approximate estimate it has been found that the conditions are such as to make the supposition of turbulence

* *Loc. cit.* † *Loc. cit.*

‡ Gibson & Grindley, Proc. Roy. Soc. A, lxxx. (1908).

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quite admissible, especially if due allowance be made for the curvature effect *.

In the case of steady motion the velocity at a given point remains constant in direction, and its magnitude varies directly as the first power of the external forces. We shall assume that in the case of turbulent motion the average velocity $\bar{u}$ is, similarly, constant in direction, but that its magnitude varies as (external forces)^y, y being <1. Then (using equations (3) and (4)),

$$\delta_2 r = \frac{\mathrm{F}}{i^2} = \frac{1}{i^2}\iiint_\Sigma \mathrm{S}u\mathrm{VHI}\,d\Sigma \propto \frac{1}{i^2}.(hi)^y.hi \propto h^{1+y}.i^{-1-y}.$$

But

$$\delta_2 r = \mathrm{B}\frac{h^2 s}{\eta}.f\left(\frac{\eta^2}{hi s\rho}\right).\phi\left(\frac{\sigma}{\sigma'}\right);$$

$$\therefore\quad f\left(\frac{\eta^2}{hi s\rho}\right) = \left(\frac{\eta^2}{hi s\rho}\right)^{1-y}.$$

Therefore the increase of resistance, δr, which, as already shown, is entirely represented by $\delta_2 r$, is given by

$$\delta r = \delta_2 r = \mathrm{B}\frac{h^{1+y}.s^y}{i^{1-y}.\eta^{2y-1}.\rho^{1-y}}\phi\left(\frac{\sigma}{\sigma'}\right). \quad . \quad . \quad . \quad (7)$$

In those experiments in which the leads extend into the part of the liquid in the field the geometry of the system is complicated, and also $\phi\left(\frac{\sigma}{\sigma'}\right)$ has to be taken into account.

In such cases formula (7) cannot be simplified. However, it can be simplified for cases of straight cylindrical columns with the leads far removed from the field. In the first place, $\phi\left(\frac{\sigma}{\sigma'}\right)$ is a constant and can be included in the constant B. The geometrical configuration of the tube is determined entirely by its diameter d. We shall suppose that the magnetic field is produced by an electromagnet having circular pole-pieces of diameter D, at a distance apart t, and that the tube passes symmetrically between the pole-pieces as shown in fig. 2.

The quantities which affect the geometry of the magnetic field in the neighbourhood of the tube are t, D, and the permeability μ; and in order to maintain geometrical similarity of the whole system, d/t, D/t, and μ must be kept constant. For reasons already given, the effect of

* An approximate calculation based on certain assumptions is given in an Appendix to the paper.

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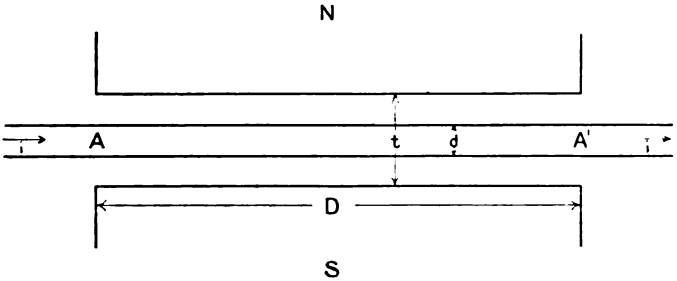
a possible variation in μ can be neglected. The motion produced in the liquid arises from the variation of HI, and as the variation of the field is practically confined to the ends A and A′ the motion will be mostly produced there. The extension of this motion from the ends into the middle of AA′ can be neglected, since in all actual cases the distance D is large compared with the diameter d of the tube. It follows that δr is independent of D. The only quantity which need be taken into account is therefore d/t, and s^y in equation (7) can be replaced by $d^y . F(d/t)$.

Fig. 2.



For small variations of d/t, $F(d/t)$ can be replaced by $(d/t)^\beta$, and it can be shown further that $0<\beta<1$. Formula (7) then reduces to

$$\delta r = B . \frac{h^{1+y} . d^{\beta+y}}{\eta^{2y-1} . \rho^{1-y} . i^{1-y} . t^\beta} . \quad . \quad . \quad . \quad (7\,a)$$

An advantage of this case over the more general case represented by (7) is that there are two additional quantities, d and t, with respect to which the variation of δr can be investigated.

Jones* has found that formula (7a) represents the variation of δr with respect to all the quantities concerned, and that formula (7) represents the results of experiments in the more complicated cases with current leads in the field and with bent tubes; the value of y in all cases is, to within experimental error, 0·59. Moreover, in several minor respects, Jones finds his observations to be in accordance with the theory.

δr, represented by formulæ (7) and (7a), is proportional to i^{y-1}. Drude and Nernst observed a variation of δr with the current, the observed δr for mercury decreasing from ·271 per cent. for i=·086 ampere to ·159 per cent. for i=318 amperes. The corresponding value of y is 0·59, which is the same as the value found by Jones.

* *Loc. cit.*

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The validity of formulæ (7) and (7*a*) substantiates the theory in general, and in particular justifies the supposition that the motion in the experiments concerned is turbulent. Certain inferences concerning the nature of this turbulent motion will now be made.

In deducing formula (7) it was supposed that the average velocity, $\bar{u}$, at a given point remains constant in direction as the external forces are varied proportionately: in other words, that the average stream-lines maintain a constant shape. If this is not so, then the dissipation F, $=\iiint_{\Sigma} S\bar{u}\mathrm{VHI}\,d\Sigma$, is affected in so far as the angle between $\bar{u}$ and VHI changes. This effect would certainly be dependent upon the actual configuration of the stream-lines, and as a result the value of y would be different for cases in which the shape of the boundary of the liquid and the distribution of the external forces are different. However, as has been already stated, y has the same value in all cases, including those with current leads in or completely out of the field, and with the liquid contained in straight or bent tubes. It can therefore be concluded that in the turbulent motion of a liquid in an enclosed space, maintained by the action of external volume forces, the average stream-lines maintain a constant shape *, and the magnitude of the average velocity, $\bar{u}$, at any point varies as (the external forces)$^{\cdot 59}$.

We can calculate from this law of the variation of the velocity the dependency of the resistance to the motion on the velocity. The average resistance to the turbulent motion of the liquid can be resolved into a system of shears, in which the shearing force, S, at any point is tangential to the average stream-line through that point. Since the stream-lines remain unaltered in shape, when the external forces are varied proportionately at all points, it follows that the geometry of the system of shears remains unaltered also. Consequently, since the shears balance the accelerating

* In this respect they resemble the stream-lines of steady motion. However, it is more or less a matter for conjecture whether the actual shape of the former is the same as that of the stream-lines of the steady motion of a liquid produced in the same enclosure by a similar system of forces. If that is the case, then there is a quantity in turbulent motion corresponding to viscosity in steady motion. In the present case the expression for such a quantity would be $K.\bar{u}^{\cdot 75}.s^{\cdot 75}.\rho^{\cdot 75}.\eta^{\cdot 25}$, K being a numerical constant depending upon the geometry of the system, $\bar{u}$ the velocity at some standard point, and s a measure of the scale of the system.

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effect of the external forces, the shear at any point must vary directly as the external forces. Now the velocities are proportional to (external forces)$^{\cdot 59}$, so that the shearing forces are proportional to (velocity)$^{\frac{1}{\cdot 59}}$, *i. e.* (velocity)$^{1\cdot 70}$. In other words, the "resistance" to the motion is proportional to (velocity)$^{1\cdot 70}$. Osborne Reynolds investigated the turbulent flow of water through straight pipes, and found that the resistance to the motion was proportional to (velocity)$^{1\cdot 72}$. The motion in Reynolds' experiments differs considerably from that which we have been considering here. The average stream-lines in the former are straight, whilst in the latter they have a radius of curvature of the order of a millimetre; also the liquid used by Reynolds was water, whilst in these electrical experiments the liquid generally used has been mercury. In spite of these differences, the laws of variation of resistance with velocity are almost identical in the two cases.

Summary.

The change in the electrical resistance of a liquid conductor due to the action of a magnetic field is attributed to the sum of (1) a true resistance change, (2) a change consequent upon energy expended in maintaining hydrodynamic currents which are shown to be produced in the liquid conductor. An expression for the latter is obtained by means of dimensional analysis.

According to the theory thus developed there is evidence, in the experimental results of Rossi, for the existence of a true resistance change in bismuth amalgams. An analysis of the results shows that a 1 per cent. bismuth amalgam gives a true increase of resistance of ·00010 per cent. in a field of 4000 gauss. Further evidence of a true effect in liquid metals is furnished by Berndt's work on molten bismuth, and in this case the estimated true change at 420° is of the order of ·002 per cent. for a field of 3000 gauss.

In other cases the hydrodynamic effect certainly predominates, and, in most cases, a true change, if present at all, is negligible.

The variation of δr with the current traversing the liquid metal conductor, an effect which has been observed in certain cases, is explained by supposing that the motion of the liquid in these cases is turbulent. The other theoretical consequences of this supposition are fully substantiated by the experimental work of T. Jones. From the nature of

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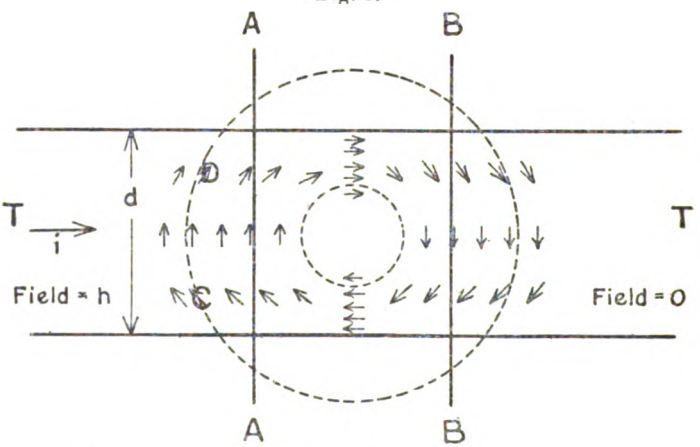
Jones's results it is shown that in the turbulent motion of liquids in an enclosed space due to the action of external volume forces, the average stream-lines maintain a constant shape as these forces are varied proportionately at all points. In this respect the average stream-lines of turbulent motion resemble the stream-lines in steady motion. The resistance to the motion is in all cases proportional to $(\text{velocity})^{1\cdot70}$, and this is in agreement with the law of resistance in turbulent motion, which has been obtained as the result of experiments under very different conditions.

In conclusion, I wish to thank Professor E. J. Evans for his valuable criticism and advice in connexion with this paper.

Appendix.

That the velocity acquired under the laws of stream-line motion is greater than than the critical velocity, can be deduced on certain assumptions. The calculation, however, only gives the order of magnitude of the velocity.

Fig. 3.



Let TT be a portion of the tube containing mercury, and AB the region where the magnetic field falls off, decreasing from its maximum value at A to a small fraction of that value at B. The volume force HI [which for the sake of argument is supposed to act upwards] is thus a constant "hI" to the left of A, and zero to the right of B. This distribution of volume force produces motion of the liquid somewhat as shown by the arrows in the diagram. In the part CD of the circuit the liquid is acted upon by a

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volume force $\frac{h.i.4}{\pi d^2}$ approximately parallel to the direction of the motion, whilst the force parallel to the motion elsewhere is small in comparison and will be neglected. We shall assume the average velocity to be equal to that which would be produced in a straight tube of diameter $d/2$ and of length l equal to that of the circuit marked by the arrows, due to the action of a pressure difference between the ends $= \frac{h.i.4 \times \mathrm{CD}}{\pi d^2} = \frac{hi4}{\pi d^2} \times \frac{d}{2}$ approximately. This velocity can be obtained by means of Poiseuille's law, and is equal to $\frac{2hid}{\pi d^2} \times \left(\frac{d}{4}\right)^2 \div 8l\eta$, where η is the viscosity of the liquid. The distance AB in the experiments concerned was about 1 cm., and l can be taken to be equal to $2+d$. The average velocity that would be produced in the case of mercury contained in a tube of diameter $d=0{\cdot}5$ cm. with a current of 0·5 amp. and a field of 1000 gauss is equal to about 3 cm. per second. The values of the various quantities given above were about the smallest used by Jones in his experiments, so that the case considered is one in which turbulence was least likely. We shall take the velocity necessary to produce turbulence to be that required in the case of motion through a tube of diameter $d/2$, the axial line of the tube being a circle of diameter d. The value in this case is probably higher than in the actual case since uniformity of shape tends to maintain steady motion.

The value of the critical velocity v_c in the case of motion through a curved tube of diameter "a," whose axis is a circle of diameter "b," can be shown to be given by

$$v_c = \frac{2000\nu}{a\left\{1+f\left(\frac{a}{b}\right)\right\}} \text{ cm. per sec.,}$$

where ν is the kinematic viscosity of the liquid and the value of $\frac{v_c a}{\nu}$ for a straight tube is taken to be 2000. In the case under consideration, $a=d/2$, $b=d$, and $d=0{\cdot}5$ cm., so that

$$v_c = 2000\nu/{\cdot}25\{1+f({\cdot}5)\}.$$

The value of this quantity when the liquid is mercury is given approximately by $\frac{10}{1+f({\cdot}5)}$ cm. per sec.

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From the value of the critical velocity for straight tubes it follows that $f(0)=0$, and from Gibson and Grindley's result it follows that $f(\cdot 01)=14$. These values indicate that $f(\cdot 5)$ is probably a large quantity, and therefore that v_c is a small fraction of 10 cm. per second. The calculated velocity is 3 cm. per second, and is therefore according to the discussion above sufficiently large to produce turbulence.

III. *The Electrical Resistance of Mercury in Magnetic Fields.* By T. J. Jones, *M.Sc.* (*Wales*), *Research Student, University College, Swansea* *.

Introduction.

THE influence of a magnetic field on the electrical resistance of mercury has been examined by a number of investigators. These have studied the effect observed when the direction of the current in the mercury is perpendicular to the magnetic field, and it is this transverse effect that will be considered in the present paper.

Drude and Nernst † (1891) observed a small increase of resistance in a column of mercury placed in a transverse magnetic field. The change of resistance increased with the field, and for a field of eight kilogauss amounted to 0·2 per cent.

Patterson ‡ (1902) obtained an increase of 0·03 per cent. in the resistance of a column of mercury for a field of twenty-five kilogauss.

Berndt § (1907) noticed that the finer the column of mercury used, the smaller the increase of resistance for a given field; and in a column of diameter 0·29 mm. and a field of three kilogauss the resistance change was only 0·00005 per cent. His work led him to conclude that the observed changes of resistance were to be attributed to what he described as "electrodynamic actions," and that if there were true magneto-resistance effects in mercury they must be exceedingly small compared with those in solid metals.

Berndt's conclusions were supported by the subsequent work of Rossi ‖ (1911) and of Nielson ¶ (1924), both of

* Communicated by Prof. E. J. Evans, D.Sc.
† Drude and Nernst, *Wied. Ann.* p. 568 (1891).
‡ Patterson, Phil. Mag. iii. p. 643 (1902).
§ Berndt, *Ann. d. Phys.* xxiii. p. 932 (1907).
‖ Rossi, *Nuov. Cimento*, ii. p. 337 (1911).
¶ Nielson, Phys. Rev. February 1924.

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whom worked on the resistance effects in fine columns. Nielson's investigations showed that the true effect (if any) in mercury must have a value less than 0·0003 per cent. for a field of sixteen kilogauss.

The above is a brief summary of the more important work done in connexion with the phenomenon of the increase of resistance in mercury due to a magnetic field.

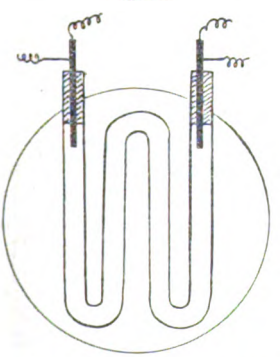
Although it may be said with some certainty, from a consideration of the above works, that the magneto-resistance effect observed in mercury is not a true effect such as is exhibited by solid metals, the nature of the effect seemed to be obscure. In the research described below, therefore, an attempt was made to throw light on the nature of the phenomenon by studying the magneto-resistance effects in fairly wide columns of mercury.

Added interest was given to the work by the development, during its course, of a theoretical investigation * of the magneto-resistance effects in liquid metals.

The Experimental Arrangement.

The magnetic fields used in the experiments were obtained with a powerful electromagnet having pole-pieces 8 cm. in diameter, and the fields were measured with a Grassot Flux-meter and exploring coils. With a current of 10 amperes the magnet gave a field of about 10 kilogauss when the poles were placed one centimetre apart, and this value of the field was the largest used in the work.

Fig. 1.



Two forms of glass tubes were used to contain the mercury—bent tubes as in fig. 1 and straight tubes as in

* By E. J. Williams, *suprà*, p. 27.

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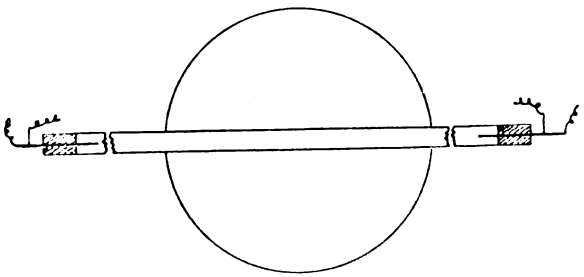
fig. 2,—the internal diameters varying from 3 to 7 mm. In the figures the circles represent the poles of the magnet, and, neglecting the stray field outside the poles, the magnetic fields act upon the portions of the mercury columns within the circles. The bent tubes enabled a longer column to be placed in the field than in the case of the straight tubes. Hence, if the magneto-resistance effect arose from a change of resistance throughout the column exposed to the field (as is the case with solid metals), then the change of resistance for a given field should be greater in the bent tube than in a straight tube of equal diameter.

Fig. 2.



The current leads into the mercury were of thick platinum wire, and the arrangement of these leads in the tubes is shown in figs. 1 and 2. It will be noticed that in the bent tubes the leads are in the magnetic field; but no correction was necessary for any resistance change which might occur in the leads due to the field, as platinum shows very small magneto-resistance effects.

In order to regulate the temperature of the mercury, a water-bath was at first used to contain the tubes; but later it was found that the bath could be dispensed with without introducing any errors into the work.

The resistance of each mercury column was low (of the order 10^{-2} ohm) and was measured by means of a Kelvin bridge. The bridge enabled a resistance change of a millionth of an ohm (*i.e.*, about 0·01 per cent. of the resistance of a mercury column) to be measured for all the columns.

In measuring the change of resistance for a given field, the following procedure was adopted: (*a*) the bridge was balanced for no field, (*b*) the magnet was excited and the bridge rebalanced, (*c*) the field was cut off and the bridge again balanced. When the reading obtained in (*c*) agreed

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with that obtained in (*a*) the change of resistance given by (*b*) was recorded.

A complete observation occupied but a few seconds; and by the above procedure any possible errors in the measurement of the resistance changes due to thermoelectric and Joule heating effects were avoided.

It will be noticed that in this work (for reasons that will be apparent later) it is the actual change of resistance, δR, that is measured and discussed, and not the relative change $\frac{\delta R}{R}$ as is usually the case in work on solid metals.

Experimental Results.

Preliminary experiments showed that the magnetoresistance effect in a column of mercury depended upon the strength of the magnetic field, the strength of the current flowing in the mercury, the diameter of the mercury column, the temperature of the mercury, and upon the distance apart of the poles of the magnet (the magnetic intensity along the axis of the gap between the poles being kept constant).

It was noticed that when the current leads into the mercury were in the magnetic field (*e.g.*, as in fig. 1), a change in the position or shape of the leads had a marked effect on the magnitude of the resistance change.

The following were other phenomena observed. When balancing the bridge with the mercury resistance in the field, it was necessary to allow the bridge current to flow for a few seconds prior to closing the galvanometer circuit, as the resistance change occupied this interval of time in attaining its full value for that particular field. This "lag" effect was found to be due to some cause in the mercury itself and not to any inductive actions in the apparatus. It was also found that even when the "lag" effect was allowed for, the resistance of the mercury column when in the field was not constant but fluctuated very slightly—this fluctuation being manifested by a slight but continual motion of the spot of light about the zero of the galvanometer scale. The greater the change of resistance due to the field, the greater were these fluctuations. However, the magnitude of the fluctuations was always less than 1 per cent. of the corresponding change of resistance.

The following experiments were made to obtain, if possible, a relation between δR and the various factors upon which it depends.

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1. *The Variation of* δR *with the Field.*

The variation of the resistance change with the field was investigated for fields ranging from 2 to 10 kilogauss and the experiments were extended to both types of tubes already described, these having diameters between 3 and 7 mm. Certain definite currents between 0·5 and 5 amperes were passed through the mercury column, and the variations of δR with the field for these currents were recorded.

The change of resistance continued to increase with the field and, up to the highest fields employed, showed no tendency to reach a constant value. It was also found that, within the above limits of the magnetic field, of the current in the mercury, and of the diameter of the mercury column, the relation between the resistance change and the field could be represented (within the limits of experimental error) by the relation

$$\delta R \propto H^{1\cdot 58}.$$

The results obtained in a typical case—that of a straight tube of diameter 5 mm.—are collected in Table I., where the first column gives the various fields in gauss, while the other columns give the corresponding resistance changes for the specified currents.

TABLE I.

Field in Gauss.	δR (ohms)×10^6 for currents ranging from 5 to 0·5 amps.								
H.	5·0.	4·0.	3·0.	2·5.	2·0.	1·5.	1·0.	·7.	·5.
2,000	5	7	8	9	10	12	15	18	23
4,200	18	21	27	30	34	40	50	55	64
7,000	55	62	69	75	82	91	110	127	148
8,000	67	74	83	89	98	111	130	153	176
8,500	77	82	92	98	107	120	145	168	193
8,900	82	88	98	105	116	130	154	181	207
9,100	85	95	104	111	123	137	164	191	219
9,600	93	99	112	122	133	149	178	207	236
10,000	98	108	120	129	142	159	188	218	248

Fig. 3 shows graphically the result of plotting (for certain vaues of the current in the mercury) the changes of resistance against the field raised to the power 1·58. Similar

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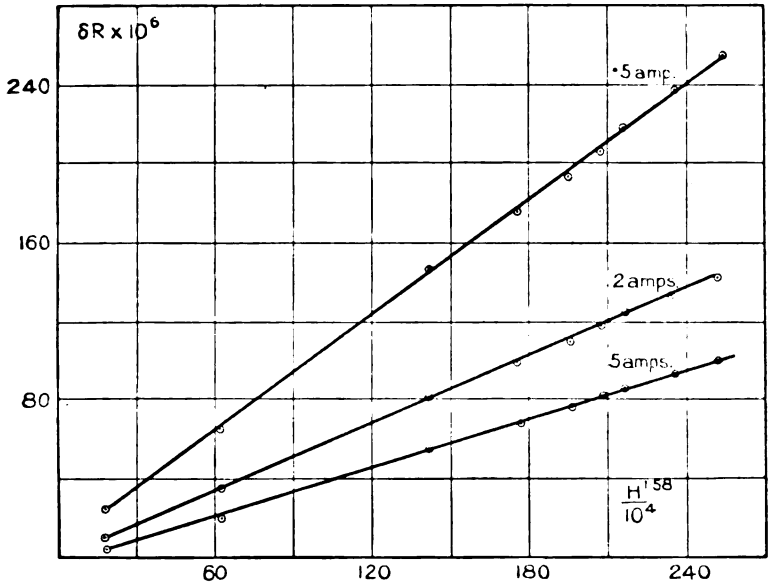
curves were obtained for all the tubes, thus indicating that the relation between δR and $H^{1\cdot58}$ is linear.

Fig. 3.



2. *The Relation between δR and the Current in the Mercury.*

The same experiments as were made in determining the relation between the resistance change and the field, for certain definite currents in the mercury, also sufficed to give the relation between the resistance change and the current.

It was found that the resistance change for a given field was greater the smaller the current in the mercury—the relation between δR and the current being given (within the limits of error) by the equation

$$\delta R \propto i^{-\cdot40}.$$

This relation holds within the range of field, current, &c., already given.

Table I. gives (for the tube mentioned above) the resistance changes for different currents between 5 and 0·5 amperes;

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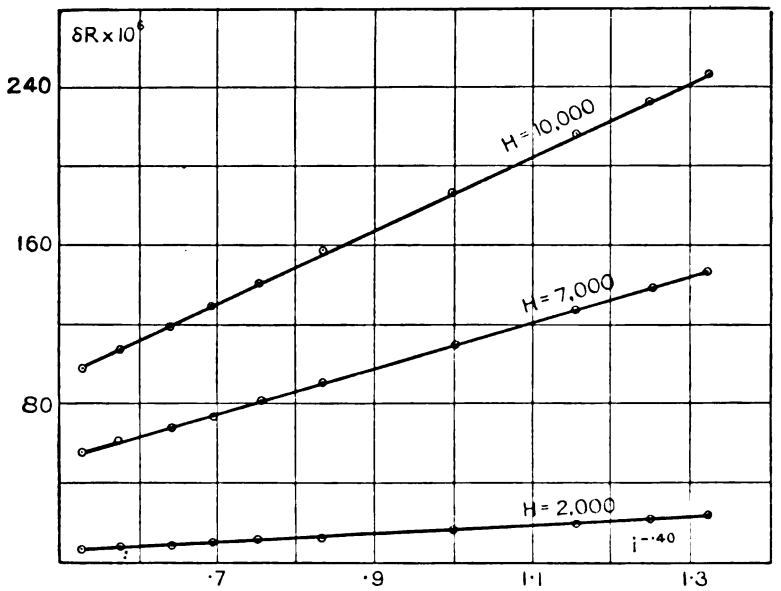
and in fig. 4 the relation between δR and the current raised to the power (minus ·40) is shown graphically. Similar curves were obtained for all the tubes.

In connexion with this "current" effect, it is interesting to note that Drude * and Nernst also observed that the change of resistance depended upon the current. Only two values of δR for two different currents are given in their paper, but these values fit in with the above relation.

Fig. 4.



As it is improbable that δR should continue to increase as the current decreases, experiments are being made to investigate (among other things) the relation between δR and the current for small currents. The results already obtained show that for currents of 1/10 ampere, or less, the relation between δR and i is not that given above, but that δR varies inversely as i raised to a power less than —0·40 and which is smaller the smaller i. It is therefore possible that for very small currents the resistance change would be independent of the current in the mercury.

* *Loc. cit.*

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3. *The Relation between* δR *and the Diameter of the Column.*

In studying the dependence of δR on the diameter of the mercury column, the resistance changes in tubes of different diameters under identical experimental conditions were compared. When the current leads into the mercury were in the magnetic field (as in the bent tubes) the position of the leads affected the resistance change to a considerable extent, and hence made it impossible to compare the values of δR for different tubes. This, together with the fact that the resistance changes in the bent tubes were found to be of about the same magnitude as those in straight tubes, caused the bent type of tube to be discarded.

The change of resistance, in straight tubes of different diameters and for a definite field and current in the mercury, are collected in Table II. There is a good agreement in the values of the ratios $\frac{\delta R}{d}$ indicating that the resistance change is proportional to the diameter of the column.

TABLE II.

δR ($\times 10^6$).	Diameter (d).	$\delta R/d$ ($\times 10^6$).
98	0·68 cm.	144
93	0·64 ,,	145
74	0·51 ,,	145
61	0·42 ,,	145
55	0·38 ,,	145
45	0·31 ,,	145

4. *The Relation between* δR *and the Distance apart of the Poles of the Magnet.*

By varying the current in the magnet, the intensity of the field along the axis of the gap between the poles could be kept constant while the distance apart of the poles was varied. Keeping the intensity constant, in this way, it was found that for tubes with leads in the field only a slight decrease occurred in δR when the poles were moved to a greater distance apart. However, when the leads were out of the influence of the field the distance apart of the poles had a marked effect upon the magnitude of the resistance change. The relation between δR and the distance b between the poles, for a constant field along the axis of the gap and for a constant current in the mercury, was

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found to be given within the error of experiment by

$$\delta R \propto \frac{1}{b^{\cdot 41}}.$$

Table III. shows the resistance changes in a long straight tube for a magnetic field of 10 kilogauss along the axis of the gap, the distance apart of the poles being varied.

TABLE III.

$\delta R\,(\times 10^6)$.	b (mm.).	$[\delta R \times b^{\cdot 41}] \times 10^6$.
93	12	257·6
97	11	258·8
100	10	257·0
105	9	258·4
110	8	258·0
116	7	257·6

It would be well here to point out that the theory of the magneto-resistance effect in mercury, which is discussed later, gives an interpretation of this dependence of δR on the distance apart of the poles. According to the theory $1/b^{\cdot 41}$ is a measure of the rate of dying away of the field outside the poles of the magnet; and it can be shown theoretically that the greater this rate of decay of the field the greater is the change of resistance for a given field along the axis of the gap between the poles of the magnet.

5. *The Dependence of* δR *upon the Position and Shape of the Leads when these were in the Field.*

In the experiments in which the current leads into the mercury were in the magnetic field (*e.g.*, fig. 1) it was noticed that altering the position or shape of the leads had a marked effect on the magnitude of the resistance change.

This "lead" effect was investigated in the following manner. A short tube (diameter 6·4 mm.) was filled with mercury and the platinum wire leads adjusted so that a column of mercury one centimetre long lay between the points of the leads. The tube was then placed in a field of 10 kilogauss and the change of resistance observed was 35×10^{-5} ohm.

A long tube of similar diameter was then filled with mercury and the wire leads placed in the tube so as to be out of the influence of the field. As the diameter of the magnet poles was eight centimetres, a column of mercury eight centimetres long lay in the magnetic field. The change of resistance for the same field and current as before was

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now only 10×10^{-5} ohm—a change much smaller than in the short column. These results show that the magneto-resistance changes are independent of the resistance of the column of mercury in the field. They also explain why it is the change of resistance, δR, and not the relative change, $\frac{\delta R}{R}$, that is considered in this work.

Again, when in the short tube mentioned above, thick copper leads which filled the tube were substituted for the wire leads, and the resistance change measured for a column of mercury one centimetre long, it was found that the change of resistance (for the same field and current as before) was only 3×10^{-6} ohm—*i. e.*, less than 1 per cent. of that obtained under similar conditions but with wire point leads.

This result, together with those preceding, seem to indicate that the resistance changes are probably due to some effects occurring in the mercury at those portions where the current enters or leaves the mercury : *i. e.*, at the leads if they are in the field, or, if the leads are not in the field, in those portions of the mercury column near the edges of the poles.

6. *The Dependence of* δR *on the Temperature.*

Experiments were made to determine the effect produced on δR by increasing the temperature of the mercury. A long glass tube containing mercury was placed in a copper bath, which in its turn was fixed between the poles of the magnet. The bath was heated by gas flames from underneath and contained first water at the room temperature (17° C.), then boiling water (100° C.), and finally boiling glycerine (290° C.). The resistance changes at these three temperatures (for given fields and current) were measured, and are collected in Table IV. The last two columns show that

TABLE IV.

δR [$\times 10^6$] at 17° C.	δR [$\times 10^6$] at 100° C.	δR [$\times 10^6$] at 290° C.	$\frac{\delta R \text{ at } 100°}{\delta R \text{ at } 17°}$.	$\frac{\delta R \text{ at } 290°}{\delta R \text{ at } 17°}$.
17	18	19	1·059	1·120
52	55	58	1·060	1·115
74	78	83	1·054	1·112
94	99	106	1·053	1·128
114	120	129	1·053	1·132

on raising the temperature from 17° C. to 100° C. the resistance change increased by about 5·6 per cent., while on heating from 17° C. to 290° C. there was an increase

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of 12·5 per cent. However, allowance must be made for the increase in δR due to the increase produced by heating in the diameter of the glass tube. This change of diameter amounted to about 0·4 per cent. on heating from room temperature to that of the boiling glycerine, so that, since δR is proportional to the diameter of the column, the effect of heating from 17° C. to 290° C. is to increase δR by 12·1 per cent., while from 17° C. to 100° C. δR increases by 5·5 per cent.

7. *The Effect of the addition of Cadmium to the Mercury.*

The effect on δR of adding cadmium to the mercury was examined for a 3 per cent. cadmium amalgam. The results for this amalgam, together with those for mercury under similar conditions, are collected in Table V. It is seen that the resistance changes in the amalgam are slightly smaller than those in the mercury—the difference being about 1 per cent. [The change in the resistance of the mercury due to the addition of the cadmium is an increase of about 20 per cent.]

TABLE V.

δR for Mercury.	δR for 3 per cent. amalgam.	$\frac{\delta R \text{ for amalgam}}{\delta R \text{ for mercury}}$.
30×10^{-6}	30×10^{6}	1·00
73 ,,	72 ,,	·99
101 ,,	100 ,,	·99
121 ,,	120 ,,	·99
126 ,,	125 ,,	·99

DISCUSSION OF RESULTS.

The experiments described above show that within certain limits the magneto-resistance change at a given temperature in a straight column of mercury with the current leads out of the influence of the field is given by

$$\delta R \propto \frac{H^{1\cdot 58} d}{i^{\cdot 40} b^{\cdot 41}},$$

where H, d, i, and b are respectively the field along the axis of the pole gap, the diameter of the column, the current in the column, and the distance apart of the poles of the magnet.

The experiments also show that the effect in mercury is of a different nature from those exhibited by solid metals; for in

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the former the resistance change for a given field is independent of the resistance in the field and is dependent on the current in the mercury, whereas in solid metals the resistance change is proportional to the resistance in the field and is independent of the current in the conductor.

A theoretical investigation of the magneto-resistance effect in liquid metals has been made by E. J. Williams. The increase of resistance of a column of mercury (or any other liquid metal) when in a magnetic field is attributed to the expenditure of energy by the electric current in maintaining mass-motion of the mercury in certain portions of the column, this motion being developed by the electrodynamic action of the magnetic field on the mercury carrying the current.

The motion of the mercury is developed at those portions of the column in the field where the magnetic field is not uniform or where the current-density is not constant. Thus in those tubes in which the leads are in the field, the current-density in the mercury about the leads is not constant so that the motion of the mercury takes place mainly about the leads. In the tubes with leads out of the field the motion is mainly produced in those portions of the column where the current enters and leaves the field—*i. e.*, at the boundaries of the pole-pieces, for at these points the field varies rapidly.

This view of the locality of the motion, and hence of the cause of the resistance change, is consistent with the conclusion arrived at in the experiments that the cause of the change of resistance is not distributed uniformly throughout the column exposed to the field.

The motion of the mercury was experimentally demonstrated by placing one of the current leads so as to just enter the free surface of a mercury column in the magnetic field. The current-density near the surface of the mercury varied considerably, and a vigorous motion of the mercury was observed.

Support for the theory was also provided by the results obtained in the experiments dealing with the effect on δR of the shape of the leads. With thick leads approximately filling the tube—a condition which ensured nearly uniform current-density in the mercury—there was practically no resistance change when the mercury was in a uniform field. The small effect that was observed may be accounted for by a possible slight non-uniformity of the current-density or of the field.

The "lag" effect described in the preliminary experiments is explained as being due to the resistance change

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not reaching its full value until the motion of the mercury reaches its full value; and this might take an appreciable time in consequence of the mass of the mercury.

Two different theoretical relations for the resistance change were obtained by Williams, one relation being based on the assumption that the motion of the mercury was steady, while the other followed from assuming the motion to be turbulent.

On the assumption that the motion of the mercury was turbulent, the following relation was obtained for the change of resistance in a straight column having the leads out of the influence of the field:

$$\delta R \propto \frac{H^{1+\gamma} d^{\beta+\gamma}}{i^{1-\gamma} \eta^{2\gamma-1} \rho^{1-\gamma} b^{\beta}}.$$

In this relation H, d, i, and b have the same significance as before, while η and ρ are respectively the viscosity and density of the mercury. β and γ are numerical constants whose values cannot be determined theoretically—although it is shown that β lies between 0 and 1.

If β and γ be given the values ·41 and 1·59 respectively, the above relation becomes

$$\delta R \propto \frac{H^{1\cdot 59} d}{i^{\cdot 41} b^{\cdot 41} \eta^{\cdot 18} \rho^{\cdot 41}},$$

which agrees well with the relation obtained experimentally when the temperature (and hence η and ρ) is constant.

In order to test the theoretical relation with respect to the dependence of δR upon the viscosity and density of the mercury, it is necessary to vary these quantities. This can be done either by altering the temperature of the mercury or (if it be assumed that the magneto-resistance effect in the amalgam is still mainly due to the motion of the liquid) by dissolving cadmium in the mercury. It should be noted, however, that only small variations of η and ρ can be made, and it is difficult to test accurately the relation between δR and these quantities.

In the experiments on the variation of δR with temperature there was an increase in δR of about 12·1 per cent. when the mercury was heated from 17° C. to 290° C., while from 17° C. to 100° C. δR increased by 5·5 per cent. From known data * on the density and viscosity of mercury at different temperatures, the theoretical change in δR due to a rise of temperature can be calculated from the formula. It is found that δR should increase by 5·5 per cent. from 17° C. to 100° C., and by 11·9 per cent. from 17° C. to

* Kaye and Laby's Tables.

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290° C. These calculated results agree within the limits of experimental error with the observed results.

The change in δR produced by a change in the temperature of the mercury can therefore be accounted for by the variation of the density and viscosity of mercury with temperature.

In the experiments with the cadmium amalgam the viscosity and density of the amalgam are different from those of mercury. The theoretical change to be expected in δR, on the assumption that the change is to be accounted for by the alteration of η and ρ, can be calculated as data on the viscosity and density of a 3 per cent. cadmium amalgam are available *.

The required data are:—

η for 3 per cent. amalgam = 1·06 η for pure mercury.
ρ for 3 per cent. amalgam = ·98 ρ for pure mercury.

From these values the theoretical change in δR is 0·5 per cent.—a result which is not inconsistent with that obtained in the experiment.

The theoretical relation is thus seen to be in good agreement with the results of experiment.

Summary.

1. The experiments have shown:—
   (*a*) That for magnetic fields varying from 2 to 10 kilogauss, the magneto-resistance change in a straight column of mercury of diameter about 0·5 cm. when the current in the column lies between 5 and 0·5 amperes, is given by

$$\delta R \propto \frac{H^{1\cdot 58} d}{i^{\cdot 40} b^{\cdot 41}},$$

   where H, d, i, and b are respectively the field, the diameter of the column, the current in the column, and the distance apart of the poles of the magnet.
   (*b*) That the change of resistance is independent of the resistance in the field.
   (*c*) That the resistance change increases with rise in temperature of the mercury.
   (*d*) That under the conditions prevailing in the experiments (wide tubes and comparatively large fields and currents) the magneto-resistance effect in mercury is mainly, if not entirely, of a different nature from those exhibited by solid metals.

* *Vide* p. 1043, vol. iv. Mellor's 'Treatise on Chemistry.'

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2. The results of the experiments have been examined from the point of view of a theory which attributes the magneto-resistance effects in mercury to the development, under the combined action of the magnetic field and the current, of mass-motion of the mercury in certain portions of the column. This theory has been found to explain all the observed phenomena and to give for the resistance change a relation which is in good agreement with that obtained in the experiments.

In conclusion, I wish to thank Professor E. J. Evans, D.Sc., and Mr. W. Morris Jones, M.A., for their most valuable help and advice in connexion with everything in the present paper.

Further, this Research was made possible by the award of a grant by the Education Committee of the Glamorgan County Council.

IV. *On the Electric Capacity of Certain Solids of Revolution.* *By* D. M. Wrinch, *M.A.* (*Oxon.*), *D.Sc.* (*Lond.*), *Lecturer at Lady Margaret Hall, Oxford* *.

Introduction.

THE problems associated with a conducting solid of revolution when it is freely charged with electricity have at present been solved in a few cases only. Beyond the spheroids, few surfaces of revolution have been treated except those which are equipotentials for prescribed sets of electric charges lying entirely within them. In these cases, the set of charges may be replaced by a Green's equivalent stratum in the well-known manner, and the equipotential surface in question may be taken as a conductor carrying the equivalent stratum as a free surface distribution of electricity. The equipotentials associated with further, more complicated, sets of charges may also be investigated and the distribution on the resulting equipotentials may then be deduced.

If, however, it is desired to solve the problems associated with a *given* surface represented by $v=0$ in the transformation of cylindrical coordinates

$$z+i\rho=\chi(u+iv),$$

z being the axis of figure, it is necessary to satisfy Laplace's

* Communicated by the Author.

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equation, which in such cases takes the form

$$\frac{d}{du}\rho\frac{dV}{du}+\frac{d}{dv}\rho\frac{dV}{dv}=0,$$

throughout the space between the conductor and the sphere at infinity.

Now in the case of the spheroid we have

$$z=(a+a_1)\cos u,$$

$$\rho=(a-a_1)\sin u,$$

given by $v=0$ in the transformation

$$z+i\rho=ae^{i(u+iv)}+a_1e^{-i(u+iv)},$$

and it results that

$$\frac{1}{\rho}\frac{d\rho}{du}=-\cot u$$

and is independent of v, and

$$\frac{1}{\rho}\frac{d\rho}{dv}=-\frac{ae^{-v}+a_1e^{v}}{ae^{-v}-a_1e^{v}}$$

and is independent of u. Solutions of Laplace's equation follow, of the form

$$\phi(u)\psi(v),$$

where $\phi(u)\psi(v)$ satisfy the subsidiary equations

$$(d^2/du^2-\cot u\, d/du-m)\,\phi(u)\quad=0,$$

$$\left(\frac{d^2}{dv^2}-\frac{ae^{-v}+a_1e^{v}}{ae^{-v}-a_1e^{v}}\frac{d}{dv}+m\right)\psi(v)=0.$$

But this method of approach to the problem by means of the separation of variables comes to an abrupt end with the spheroid. In general the surface of revolution is represented by the zero v-level in the transformation *

$$z+i\rho=ae^{i(u+iv)}+a_1e^{i\alpha_1-i(u+iv)}+a_2e^{i\alpha_2-2i(u+iv)}+\ldots$$

(with certain restrictions on the parameters (a_n, α_n)), and we therefore have the equation in the form

$$\frac{d^2V}{du^2}+P\frac{dV}{du}+\frac{d^2V}{dv^2}+Q\frac{dV}{dv}=0,$$

* *Vide* a forthcoming paper by the present writer, "Some Boundary Problems of Mathematical Physics," Proc. London Math. Soc.

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where

$$P = \frac{[ae^{-v}\cos u - a_1 e^{v}\cos(\alpha_1 - u) - 2a_1\cos(\alpha_2 - 2u) - \ldots]}{[ae^{-v}\sin u + a_1 e^{v}\sin(\alpha_1 - u) + \ldots]},$$

$$Q = -\frac{[ae^{-v}\sin u - a_1 e^{v}\sin(\alpha_1 - u) - 2a_1\sin(\alpha_2 - 2u)\ldots]}{[ae^{-v}\sin u + a_1 e^{v}\sin(\alpha_1 - u) + \ldots]},$$

and the possibility of the separation of variables u and v has obviously entirely disappeared in all the cases beyond the spheroid, where it is not the case that

$$a_2 = a_3 \ldots = 0.$$

We therefore have to contemplate in these cases solutions in mixed functions, of type

$$\phi(u, v).$$

Progress in determining such functions associated with the various solids of revolution, which present themselves in orderly array as different choices of the parameters (a_n, α_n) are made, will evidently be increasingly difficult as the coefficients P and Q become more and more complicated. For this reason we select for consideration on this occasion the surfaces which form the zero v-level in the transformation

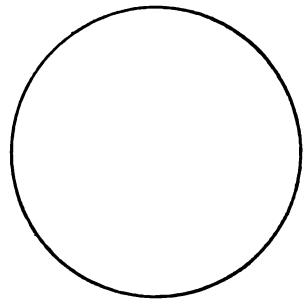
$$z + i\rho = a\left[e^{i(u+iv)} + ke^{-2i(u+iv)}\right] \quad 0 \leq k \leq \tfrac{1}{2}.$$

These surfaces have as their generating curves the simple closed nodeless epicyclics of retrograde type,

$$\left.\begin{aligned} x &= a(\cos u + k\cos 2u) \\ y &= a(\sin u - k\sin 2u), \end{aligned}\right\} \quad 0 \leq k \leq \tfrac{1}{2}$$

which range from the circle for $k=0$ to the three-cusped hypocycloid for $k=\frac{1}{2}$, the restriction, $k \leq \frac{1}{2}$, being evidently

Fig. 1.



k = 0

necessary in order that the curves shall not have intersecting branches.

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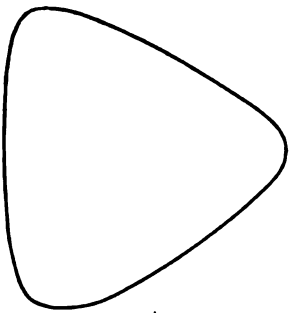
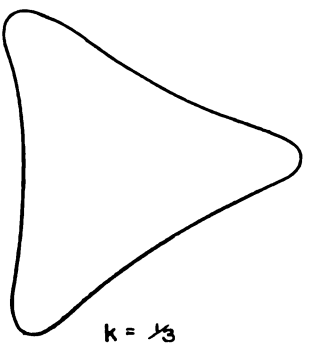
Fig. 2.



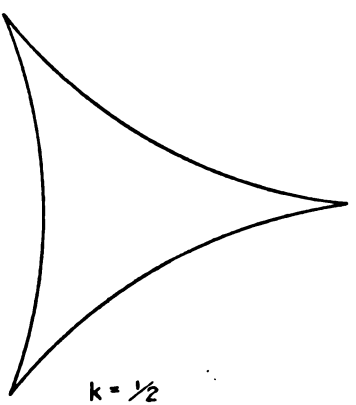
$k = \frac{1}{5}$

Fig. 3.



$k = \frac{1}{3}$

Fig. 4.



$k = \frac{1}{2}$

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We are able to obtain an expression for the potential when these conductors are maintained at potential unity in the form

$$V = f_0(u, e^v) + kf_1(u, e^v) + k^2 f_2(u, e^v) + \ldots,$$

and as many of the functions f_n as are required can be calculated. The capacity of the conductor can also be obtained in the form

$$C = a({}_1a_0 + {}_1a_2k^2 + {}_1a_4k^4 + \ldots).$$

For practical purposes it will, in general, be sufficient to use the approximation given in this paper, namely

$$C = a(1 - \cdot 06857\,k^2 - \cdot 00559\,k^4),$$

an approximation which is correct to at least 1 in 64, terms in k^6 alone being neglected.

The problem under consideration in this paper is the potential of the solid of revolution given by

$$\left.\begin{aligned} z &= a(\cos u + k\cos 2u) \\ \rho &= a(\sin u - k\sin 2u) \end{aligned}\right\} \quad 0 \leq k \leq \tfrac{1}{2}$$

when it is freely charged to potential unity.

The generating curve is a closed nodeless epicyclic of retrograde type, sometimes also called a hypotrochoid.

Consider the transformation

$$z + i\rho = a(e^{iw} + ke^{-2iw}),$$

with

$$w = u + iv.$$

The surface of the solid is given by $v = 0$ and the sphere at infinity by $v = -\infty$. Now the potential V must be equal to unity on $v = 0$ and must vanish at $v = -\infty$. Further, for values of v intermediate between zero and $-\infty$, V must be without singularities and satisfy Laplace's equation $\nabla^2 V = 0$. Laplace's equation in the variables z and ρ becomes

$$\frac{d}{du}\rho\frac{dV}{du} + \frac{d}{dv}\rho\frac{dV}{dv} = 0,$$

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which may be written

$$(e^{-v}\sin u - ke^{2v}\sin 2u)\left(\frac{d^2V}{du^2}+\frac{d^2V}{dv^2}\right)$$
$$+(e^{-v}\cos u - 2ke^{2v}\cos 2u)\frac{dV}{du}$$
$$-(e^{-v}\sin u + 2ke^{2v}\sin 2u)\frac{dV}{dv} = 0,$$

or

$$\frac{1}{\sin u}\frac{d}{du}\sin u\frac{dV}{du}+\frac{d^2V}{dv^2}-\frac{dV}{dv}$$
$$= ke^{3v}\left\{\frac{1}{\sin u}\frac{d}{du}\sin 2u\frac{dV}{du}+2\cos u\right\}\left(\frac{d^2V}{dv^2}+2\frac{dV}{dv}\right).$$

Using the coordinates μ and η given by

$$\mu = \cos u,$$
$$\eta = e^v,$$

as will from time to time be convenient, we have the equation in the form

$$\frac{d}{d\mu}(1-\mu^2)\frac{dV}{d\mu}+\eta^2\frac{d^2V}{d\eta^2}$$
$$= k\left(2\eta^3\frac{d}{d\mu}\mu(1-\mu^2)\frac{dV}{d\mu}+2\mu\eta^2\frac{d}{d\eta}\eta^3\frac{dV}{d\eta}\right).$$

In terms of η, the surface of the conductor is given by $\eta=1$ and the sphere at infinity by $\eta=0$.

Introducing operators given by

$$D \equiv \frac{d}{d\mu}(1-\mu^2)\frac{d}{d\mu}+\eta^2\frac{d^2}{d\eta^2},$$
$$E \equiv 2\eta^3\frac{d}{d\mu}\mu(1-\mu^2)\frac{d}{d\mu}+2\mu\eta^3\frac{d}{d\eta}\eta^3\frac{d}{d\eta},$$

the equation for V may be written in the form

$$D\,.\,V = kE\,.\,V.$$

Now the degenerate case $k=0$ represents the sphere and the equation for V then reduces to

$$D\,.\,V = 0.$$

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This equation has the solutions

$$\sum_0^\infty P_n(\mu)(a_n\eta^{n+1}+b_n\eta^{-n}),$$

and, in particular, solutions evanescent on the sphere at infinity are given by

$$\sum_0^\infty a_n P_n(\mu)\eta^{n+1}.$$

Now, in this degenerate case, we have

$$V = P_0\eta = \eta$$

when the sphere is freely charged to potential unity. The general case under consideration in this paper may evidently therefore be treated by assuming for V the form

$$V = f_0(\mu, \eta) + kf_1(\mu, \eta) + k^2 f_2(\mu, \eta) + \ldots$$

with

$$f_0(\mu, \eta) = \eta.$$

By allowing only positive powers of η in the various functions f_n, we at once ensure that V shall be evanescent at infinity.

The form assumed for V will be satisfactory, so far as the satisfying of Laplace's equation is concerned, provided that

$$D \,.\, f_{n+1} = E \,.\, f_n,$$

and if we are able in addition to select for the functions f_n functions which vanish on $\eta=1$, the conditions of the problem are satisfied, the restriction, to positive powers of η only, having already ensured that V is evanescent at infinity.

We consider first the equation for f_1, namely

$$D \,.\, f_1 = E \,.\, f_0 = 6\eta^4 P_1.$$

A particular integral is given by

$$\tfrac{3}{5} P_1(\mu)\eta^4,$$

and the complementary function—which is evidently shared by all the f_n functions—is

$$\Sigma a_n P_n(\mu)\eta^{n+1}.$$

Thus a solution which vanishes on $\eta=1$ is obtained in the form

$$f_1(\mu, \eta) = \tfrac{3}{5} P_1(\mu)(\eta^4-\eta^2).$$

We therefore have

$$V = \eta + \tfrac{3}{5} kP_1(\mu)(\eta^4-\eta^2),$$

terms in k^2 being neglected.

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The equation for f_2 in the same way is given by

$$D \,.\, f_2 = \tfrac{3}{5} E(P_1(\eta^4 - \eta^2)),$$

and it will be worth while to consider at once the effect of the operator E on products of P_n functions and powers of η We have

$$\begin{aligned}
E \,.\, P_n(\mu)\eta^s &= 2\eta^{s+3}\left\{\frac{d}{d\mu}\mu(1-\mu^2)\frac{dP_n}{d\mu} + \mu s(s+2)P_n\right\} \\
&= 2\eta^{s+3}\left\{(1-\mu^2)\frac{dP_n}{d\mu} - \mu n(n+1)P_n + \mu s(s+2)P_n\right\} \\
&= 2\eta^{s+3}\left\{nP_{n-1} - nP_n - \mu n(n+1)P_n + \mu s(s+2)P_n\right\} \\
&= 2\eta^{s+3}\left\{nP_{n-1} + (s-n)(s+n+2)\mu P_n\right\} \\
&= 2\eta^{s+3}\left\{nP_{n-1} + \frac{(s-n)(s+n+2)}{2n+1}[(n+1)P_{n+1} \right. \\
&\qquad\qquad \left. + nP_{n-1}]\right\} \\
&= \frac{2}{2n+1}\eta^{s+3}\left\{n(s-n+1)(s+n+1)P_{n-1} \right. \\
&\qquad\qquad \left. + (n+1)(s-n)(s+n+2)P_{n+}\right\}
\end{aligned}$$

Now consider the effect of the operator D on a similar product. We have

$$\begin{aligned}
D \,.\, P_\nu(\mu)\eta^\sigma &= [\sigma(\sigma-1) - \nu(\nu+1)]P\nu\mu^\sigma \\
&= (\sigma+\nu)(\sigma-\nu-1)P_\nu\mu^\sigma.
\end{aligned}$$

Thus if $f_r(\mu, \eta)$ is of the form

$$f_r(\mu, \eta) = \Sigma b_{n,s} P_n(\mu)\eta^s,$$

it follows that

$$\begin{aligned}
D \,.\, f_{r+1}(\mu, \eta) &= E \,.\, f_r(\mu, \eta) \\
&= \Sigma \frac{2\eta^{s+3}}{2n+1} b_{n,s}\{n(s-n+1)(s+n+1)P_{n-1} \\
&\qquad\qquad + (n+1)(s-n)(s+n+2)P_{n+1}\},
\end{aligned}$$

and we have at once a particular integral for f_{r+1} in the form

$$\Sigma \frac{2\eta^{s+3}}{2n+1} b_{n,s}\left\{\frac{n(s-n+1)(s+n+1)}{(s-n+3)(s+n+2)}P_{n-1} \right. \\ \left. + \frac{(n+1)(s-n)(s+n+2)}{(s-n+1)(s+n+4)}P_{n+1}\right\}.$$

With the help of the complementary function we then

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obtain a solution which vanishes on $\eta=1$ in the form

$$f_{r+1}(\mu,\eta) = \Sigma \frac{2}{2n+1} b_{n,s} \left\{ \frac{n(s-n+1)(s+n+1)}{(s-n+3)(s+n+2)} (\eta^{s+3}-\eta^{n}) + \frac{(n+1)(s-n)(s+n+2)}{(s-n+1)(s+n+4)} (\eta^{s+3}-\eta^{n+2}) \right\}.$$

These results make it possible to write down the various functions f_n one at a time. The types of terms which occur in the functions f_0, f_1 ... are as follows :—

$$f_0(\mu,\eta) = {}_1a_0\eta P_0,$$

$$f_1(\mu,\eta) = P_1({}_4a_1\eta^4 + {}_2a_1\eta^2),$$

$$f_2(\mu,\eta) = P_0({}_7a_2\eta^7 + {}_5a_2\eta^5 + {}_1a_2\eta) + P_2({}_7b_2\eta^7 + {}_5b_2\eta^5 + {}_3b_2\eta^3),$$

$$f_3(\mu,\eta) = P_1({}_{10}a_3\eta^{10} + {}_8a_3\eta^8 + {}_6a_3\eta^6 + {}_4a_3\eta^4 + {}_2a_3\eta^2) + P_3({}_{10}b_3\eta^{10} + {}_8b_3\eta^8 + {}_6b_3\eta^6 + {}_4b_3\eta^4),$$

$$f_4(\mu,\eta) = P_0({}_{13}a_4\eta^{13} + {}_{11}a_4\eta^{11} + {}_9a_4\eta^9 + {}_7a_4\eta^7 + {}_5a_4\eta^5 + {}_1a_4\eta) + P_2(\ldots) + P_4(\ldots).$$

The surface density of electrification, σ, at any point u on the conductor is given in the form

$$4\pi\sigma = -\frac{\partial V}{\partial v} \Big/ \frac{ds}{du} = -\eta \frac{\partial V}{\partial \eta} \Big/ \left| \frac{ds}{du} \right|,$$

where ds is the element of arc of the generating curve, so that

$$(ds/du)^2 = a^2\{\sin u + 2k \sin 2u)^2 + (\cos u - 2k \cos 2u)^2\}$$
$$= a^2(1 - 4k \cos 3u + 4k^2).$$

Thus

$$4\pi\sigma = -\left\{ \eta \frac{\partial}{\partial \eta} (f_0(\mu,\eta) + kf_1(\mu,\eta) + \ldots) \right\}_{\eta=1} \Big/ \left| \frac{ds}{du} \right|,$$

where $\cos u = \mu$.

To find the capacity of the conductor we have to obtain the total charge E on the conductor. Now as $r \to \infty$, $V \to E/r$. But

$$r^2 = \frac{a^2}{\eta^2} + a^2\eta k \cos 3u + \tfrac{1}{4}a^2\eta^4,$$

so that

$$r = \frac{a}{\eta} + \text{terms in } \eta, \eta^2 \ldots$$

Thus

$$E/a = \operatorname*{lt}_{\eta \to 0} V/\eta$$
$$= {}_1a_0 + {}_1a_2k^2 + {}_1a_4k^4 + \ldots.$$

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Since the conductor is maintained at unit potential the capacity is given by E itself, so that

$$C = a\{{}_1a_0 + {}_1a_2k^2 + {}_1a_4k^4 + {}_1a_6k^6 + \ldots\}.$$

Since k ranges between unity and one-half, it will be sufficient for practical purposes to use the approximation

$$C = a({}_1a_0 + {}_1a_2k^2 + {}_1a_4k^4),$$

which neglects terms in k^6 and so gives an accuracy of at least 1 in 64. In the case of curves of cross-section which approximate more nearly to the sphere, the accuracy of this approximation will be considerably greater.

To find the coefficients necessary for this evaluation we proceed as follows. We already have

$${}_1a_0 = 1, \quad {}_4a_1 = \tfrac{3}{5}, \quad {}_2a_1 = -\tfrac{3}{5}.$$

Then in view of the derivation of terms in each f_n function from terms given in the preceding function f_{n-1}, we have the following relations :—

$$\text{I.} \quad \begin{aligned}
{}_{13}a_4 &= \tfrac{10}{13} \cdot \tfrac{2}{3}\, {}_{10}a_3, \\
{}_{11}a_4 &= \tfrac{8}{11} \cdot \tfrac{2}{3}\, {}_8a_3, \\
{}_9a_4 &= \tfrac{6}{9} \cdot \tfrac{2}{3}\, {}_6a_3, \\
{}_7a_4 &= \tfrac{4}{7} \cdot \tfrac{2}{3}\, {}_4a_3, \\
{}_5a_4 &= \tfrac{2}{5} \cdot \tfrac{2}{3}\, {}_2a_3, \\
-{}_1a_4 &= {}_{13}a_4 + {}_{11}a_4 + {}_9a_4 + {}_7a_4 + {}_5a_4.
\end{aligned}$$

$$\text{II.} \quad \begin{aligned}
{}_{10}a_3 &= \tfrac{7}{8} \cdot \tfrac{9}{11} \cdot \tfrac{2}{1}\, {}_7a_2 + \tfrac{6}{8} \cdot \tfrac{10}{11} \cdot \tfrac{4}{5}\, {}_7b_2, \\
{}_8a_3 &= \tfrac{5}{6} \cdot \tfrac{7}{9} \cdot \tfrac{2}{1}\, {}_5a_2 + \tfrac{4}{6} \cdot \tfrac{8}{9} \cdot \tfrac{4}{5}\, {}_5b_2, \\
{}_6a_3 &= \qquad\qquad\qquad \tfrac{2}{4} \cdot \tfrac{6}{7} \cdot \tfrac{4}{5}\, {}_3b_2, \\
{}_4a_3 &= \tfrac{1}{2} \cdot \tfrac{3}{5} \cdot \tfrac{2}{1}\, {}_1a_2, \\
-{}_2a_3 &= {}_{10}a_3 + {}_8a_3 + {}_6a_3 + {}_4a_3.
\end{aligned}$$

$$\text{III.} \quad \begin{aligned}
{}_7a_2 &= \tfrac{4}{7} \cdot \tfrac{2}{3}\, {}_4a_1, \\
{}_5a_2 &= \tfrac{2}{5} \cdot \tfrac{2}{3}\, {}_2a_1, \\
-{}_1a_2 &= {}_7a_2 + {}_5a_2, \\
{}_7b_2 &= \tfrac{3}{4} \cdot \tfrac{7}{9} \cdot \tfrac{4}{5}\, {}_4a_1, \\
{}_5b_2 &= \tfrac{1}{2} \cdot \tfrac{5}{7} \cdot \tfrac{4}{5}\, {}_2a_1, \\
-{}_3b_2 &= {}_7b_2 + {}_5b_2.
\end{aligned}$$

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Then after reduction we obtain the results

$$ {}_1a_2 = -12/175 = -\cdot 06857, $$

$$ {}_1a_4/{}_4a_1 = -(16 \times 563320) / (25 \times 35^2 \times 9 \times 13 \times 27) $$

$$ = -\cdot 09316 ; $$

$$ \therefore \quad {}_1a_4 = -\cdot 00559. $$

Thus

$$ C = a(1 - \cdot 06857\, k^2 - \cdot 00559\, k^4), $$

terms in k^6 being neglected.

It is further possible to solve the problem of these conductors in a uniform field of force, or any other electric field, by application of the type of analysis which has been developed in this paper.

Summary.

The problem associated with a conducting solid of revolution when it is freely charged with electricity, which have at present been solved only for the spheroid and a few isolated cases, are discussed in this paper for solids whose generating curves are certain closed nodeless epicyclics of retrograde type with equation

$$ \left.\begin{aligned} z &= a(\cos u + k \cos 2u) \\ \rho &= a(\sin u - k \sin 2u), \end{aligned}\right\} \quad 0 \leq k \leq \tfrac{1}{2} $$

which range from the circle, for $k=0$, to the three-cusped hypocycloid, for $k=\frac{1}{2}$. The potential when such a solid is freely charged is expressed in *mixed* functions in the form

$$ V = f_0(u, e^v) + kf_1(u, e^v) + k^2 f_2(u, e^v) \ldots, $$

the coordinates u and v being specified by the transformation

$$ z + i\rho = a(e^{iw} + ke^{-2iw}) $$

with

$$ w = u + iv, $$

and the capacity of the conductor results in the form

$$ C = a\{{}_1a_0 + {}_1a_2 k^2 + {}_1a_4 k^4 + \ldots\}. $$

The approximation given in this paper, viz.

$$ C = a\{1 - \cdot 06857\, k^2 - \cdot 00559\, k^4\}, $$

is correct to at least 1 in 64.

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V. *On Transient Electric Phenomena in a Non-Inductive Circuit.* By J. A. WILCKEN, *B.Sc., Ph.D., Lecturer in Electrical Engineering at Armstrong College, Newcastle-upon-Tyne* *.

IT is known that the discussion of the electric phenomena in a so-called non-inductive circuit, containing capacity and resistance only, with rigorous exclusion of inductance, leads to the inconsistency of an instantaneous rise of current, from zero to a finite value, on closing the switch †, and it would thus appear that the observed transients can only be accounted for by the presence of a certain amount of inductance which, however small, appreciably affects the current and voltage for a very short time after closing or opening the circuit, though without any measurable influence under steady conditions, such as obtain in a system supplied with continuous current. Obviously, the influence of even a very small inductance becomes farther enhanced in the case of alternating currents, through the frequency-factor.

Mathematically, the problem turns on the integration of the differential equation

$$e = \mathrm{L}\frac{di}{dt} + ri + \frac{1}{\mathrm{C}}\int idt \quad . \quad . \quad . \quad . \quad (1)$$

in the case of L being small. For the sake of physical interpretation, however, the magnitude of L must be compared with other quantities of the same dimensions. In the usual notation, we have,

L, inductance	—	dimension	$[l]$
r, resistance	—	,,	$[lt^{-1}]$
C, capacity	—	,,	$[l^{-1}t^2]$,

and the smallness of the inductance may thus be adequately expressed in terms of the numerical fraction $\mathrm{L}/r^2\mathrm{C}$.

We consider first the case of a constant impressed electromotive force e, $de/dt = 0$, and derive the equation

$$\mathrm{L}\frac{d^2i}{dt^2} + r\frac{di}{dt} + i/\mathrm{C} = 0, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

* Communicated by the Author.

† Steinmetz, 'Transient Electric Phenomena,' p. 55, McGraw-Hill, 1920.

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the general solution of which can be written in the usual exponential form,

$$i = A\epsilon^{\alpha_1 t} + B\epsilon^{\alpha_2 t}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

α_1 and α_2 being the roots of the quadratic

$$L\alpha^2 + r\alpha + 1/C = 0. \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The potential difference at the condenser terminals is now obtained from (1),

$$e_1 = e - ri - L\frac{di}{dt}, \quad . \quad . \quad . \quad . \quad . \quad (5)$$

and the initial conditions,

$$\left.\begin{aligned} i\,|^{t=0} &= i_0, \\ e_1\,|^{t=0} &= e_0, \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

determine the constants of integration,

$$\left.\begin{aligned} A &= \{e - e_0 - (r + \alpha_2 L)i_0\}/(\alpha_1 - \alpha_2)L, \\ B &= -\{e - e_0 - (r + \alpha_1 L)i_0\}/(\alpha_1 - \alpha_2)L. \end{aligned}\right\} \quad . \quad . \quad (7)$$

As the fraction L/r^2C decreases indefinitely, the root

$$\alpha_1 = (-r + \sqrt{r^2 - 4L/C})/2L$$

assumes the indeterminate form 0/0, and the general solution ceases to have any meaning. Steinmetz gives special attention to this case (*l. c.*), but, through a somewhat careless omission of small quantities, arrives at an expression,

$$i = (1/r)\{(e - e_0)\epsilon^{-t/rC} - (e - e_0 - ri_0)\epsilon^{-rt/L}\}, \quad . \quad (8)$$

which, on substitution in the left-hand side of equation (2), gives

$$\{(L/r^2C)(e - e_0)\epsilon^{-t/rC} - (e - e_0 - ri_0)\epsilon^{-rt/L}\}/rC,$$

a quantity which is not negligible for all values of t unless both L/r^2C and $e - e_0 - ri_0$ are very small. The deductions obtained are therefore not to be trusted without a more careful scrutiny, and in this investigation a slightly different method has been adopted, leading to conclusions at variance with Steinmetz's results, especially for very small time-intervals.

When L/r^2C is a small number, squares of which may be neglected, the finite root of equation (4) is approached by taking

$$\alpha = -1/rC,$$

a farther approximation being

$$\alpha = -1/rC - L/r^3C^2 \text{ etc.}$$

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We confine the discussion to the first approximation, and take

$$i = u\epsilon^{\alpha t},$$

u being a function of t subject to

$$L\frac{d^2u}{dt^2} + (r + 2\alpha L)\frac{du}{dt} = 0;$$

$$\therefore \quad u = A\epsilon^{(-r/L-2\alpha)t} + B, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

and so,

$$i = A\epsilon^{(1/rC-r/L)t} + B\epsilon^{-t/rC}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

$$e_1 = e - (L/rC)A\epsilon^{(1/rC-r/L)t} - (r - L/rC)B\epsilon^{-t/rC}. \quad (11)$$

Writing $\eta = L/r^2C$, the boundary conditions (6) give,

$$\left.\begin{aligned} A &= \{-(e-e_0)/r + (1-\eta)i_0\}/(1-2\eta), \\ B &= \{(e-e_0)/r - \eta i_0\}/(1-2\eta), \end{aligned}\right\} \quad . \quad (12)$$

and thus finally, neglecting higher powers of η,

$$i = \{(1+\eta)i_0 - (1+2\eta)(e-e_0)/r\}\epsilon^{(1-1/\eta)t/rC}$$
$$- \{\eta i_0 - (1+2\eta)(e-e_0)/r\}\epsilon^{-t/rC}, \quad (13)$$

$$e_1 = e(1-\epsilon^{-t/rC}) + \eta(e - e_0 - ri_0)(\epsilon^{(1-1/\eta)t/rC} - \epsilon^{-t/rC}). \quad . \quad (14)$$

If the circuit is initially dead, $i_0=0$, $e_0=0$, the values become

$$i = (1+2\eta)(e/r)(\epsilon^{-t/rC} - \epsilon^{(1-1/\eta)t/rC}, \quad . \quad . \quad (15)$$

$$e_1 = e(1-\epsilon^{-t/rC}) + \eta e(\epsilon^{(1-1/\eta)t/rC} - \epsilon^{-t/rC}). \quad . \quad (16)$$

For comparison, the curves representing the growth of current and potential on charging a condenser to 1000 volts are shown in figs. 1 and 2, for an initially dead circuit with the constants $r=200$ ohms, $C=10^{-5}$ farad, and $L=4\times10^{-3}$ henry, giving $\eta=0{\cdot}01$.

Our equations (15) and (16) become

$$i = 5{\cdot}1(\epsilon^{-500t} - \epsilon^{-49500t}), \quad . \quad . \quad . \quad . \quad (17)$$

$$e_1 = 1000(1-\epsilon^{-500t}) - 10i/5{\cdot}1, \quad . \quad . \quad . \quad (18)$$

whereas Steinmetz's formulæ would give

$$i = 5(\epsilon^{-500t} - \epsilon^{-50000t}), \quad . \quad . \quad . \quad . \quad . \quad (19)$$

$$e_1 = 1000(1-\epsilon^{-500t}). \quad . \quad . \quad . \quad . \quad . \quad (20)$$

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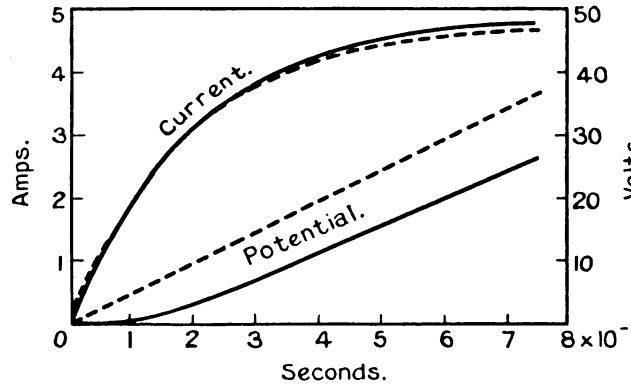
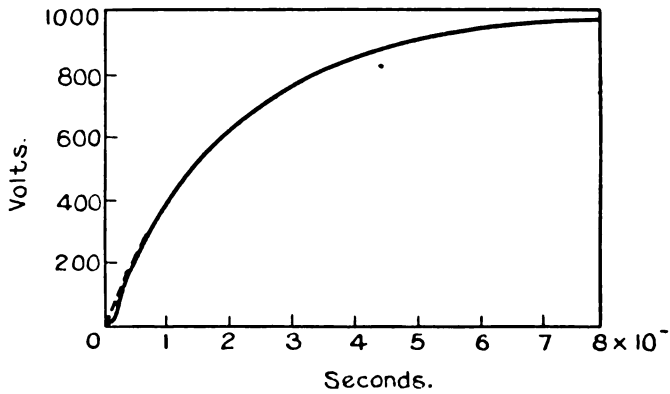
Dotted lines represent the results obtained from equations (19) and (20), while full lines connect values deduced from (17) and (18). A portion of the potential curves is also shown in fig. 1 in order to bring out more clearly the different character of the two results during the first five hundred-thousandths of a second.

Fig. 1.



The growth of current and potential in a non-inductive circuit.

Fig. 2.



The growth of potential in a non-inductive circuit.

It is seen from these diagrams that, as far as the current-values are concerned, the more accurate formula (17) gives somewhat higher values—about 2 per cent.—than (19) except at the very beginning. The current rises rapidly, attaining to 90 per cent. of its final value within five hundred-thousandths of a second.

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According to Steinmetz, the growth of potential is nearly linear for the first two-hundred thousandths of a second, but the more accurate formula (18) shows an entirely different mode of building up, the rise being very slow at first and then gradually increasing to a nearly constant slope from about the third hundred-thousandth of a second. The later portions of the two curves are nearly identical and in both cases the potential reaches 90 per cent. of its final value within five thousandths of a second.

The more gradual rise in potential is worth noting, for various reasons. Theoretically, it is interesting to observe the continuity not only of e itself, but also of its gradient de/dt, at the transition point $t=0$. Practically, the results are important in connexion with the effect of a unidirectional surge, on an overhead transmission line, caused by a lightning discharge suddenly raising the potential at one point of the line and giving rise to a single pulse of high voltage. The first portion of our potential curve in fig. 1 shows that the wave-front of such an impulse is gradually rising and so arrives without shock, whereas Steinmetz's result implies an abrupt rise of the wave-front, a condition which evidently increases the danger considerably.

VI. *Reverberation Equations for Two Adjacent Rooms connected by an Incompletely Soundproof Partition.* *By* A. H. Davis, *D.Sc.* (*From the National Physical Laboratory**.)

THE subject of this paper is closely related to a method of measuring the transmission of sound through a partition of a given material. In such a test the partition is built between two otherwise soundproof chambers. In one of the rooms, which is large and reverberant, an organ-pipe is sounded and after a time is suddenly stopped. Note is made of the length of time for which the residual sound is audible both in the source room and in that separated from it by the test partition.

W. C. Sabine † and P. E. Sabine ‡ working on these lines have determined the difference in intensity in two such rooms when different thicknesses of various partitions were used. The present paper, on the basis of a reverberation hypothesis, investigates the manner in which the general

* Communicated by the Author.

† W. C. Sabine, 'Collected Papers,' p. 237 (1922).

‡ P. E. Sabine, Phys. Rev. xxi. p. 480 (1923). 'Am. Architect,' July 28, 1920; Sept. 28, 1921; July 4, 1923.

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duration of audibility in the two rooms in such a test may depend upon the circumstances of the experiment and the transmission factor for the partition.

The decay of sound in a single room has been considered by W. C. Sabine * and by Jäger †. More recently Eckhardt ‡ has published a treatment due to Buckingham. In all cases it is recognized that a sound suffers some two or three hundred reflexions before it finally dies away, and in consequence, by random arrangement, the sound energy rapidly becomes uniformly distributed throughout the enclosure. Interference phenomena are ignored, and so results are valid only to the extent to which this is justifiable.

Buckingham assumes that the sound energy is divided up into a large number of equal parts, and that in the steady state these energy units are uniformly distributed throughout the room, both with regard to position and direction of motion. Each is assumed to move with the velocity v of sound. He shows that if the intensity of sound in the room be I (*i.e.* I energy units per unit volume) the number reaching any element of boundary surface dS in unit time is $\frac{1}{4}v.dS.I$. Of this energy a fraction will be absorbed or transmitted and the remainder reflected back into the room.

Using this result, we may readily derive differential equations governing the general intensity of sound in two adjacent rooms connected by an imperfectly soundproof partition when a source is sounded in one of them.

Let W represent the area of the test partition; k the (unknown) fraction of incident energy which is transmitted through the partition on incidence; V, V_1 the volumes of the source and test rooms respectively; S, S_1 the respective total areas of exposed surface (including the partition area); a, a_1 the mean § fractions of incident energy which are lost by the room at each reflexion through absorption or through transmission elsewhere; E the energy emission from the source in unit time.

Then, on the basis of the above reverberation theory,

* W. C. Sabine, 'Collected Papers,' p. 3 (1922).

† Jäger, *Akad. Wiss. Wien, Ber.* 120. p. 613 (1911). See 'Science Abstracts,' p. 17 (1912).

‡ Eckhardt, Frank. Inst. J. 195. p. 799 (1923).

§ If in the room there are surfaces S′, S″, S‴ etc. having respectively coefficients a', a'', a''' etc., then $aS=a'S'+a''S''+a'''S'''+$ We may note here that for highly absorbent surfaces or highly transmissive openings, with dimensions which are small compared with the wave-length of the sound, effective areas may differ somewhat from actual values owing to diffraction effects (*cf.* P. E. Sabine, Phys. Rev. **xix.** p. 402, 1922).

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if the intensities in the two rooms be I and I_1 respectively, the diminution of energy in the source room due to its total surface S is $\frac{1}{4}vaSI$ units per second; the energy received in the second room in unit time by transmission through the partition area W is $\frac{1}{4}vkWI$; the energy transmitted back to the source room from the second room in unit time is $\frac{1}{4}vkWI_1$; the rate of diminution of energy in the second room is $\frac{1}{4}va_1S_1I_1$. Consequently, the following differential equations represent the energy growth in the rooms at any instant.

Source Room $$V\frac{dI}{dt}+\frac{vaS}{4}I=E+\frac{vkW}{4}I_1, \quad . \quad . \quad . \quad . \quad (1)$$

Second Room $$V_1\frac{dI_1}{dt}+\frac{va_1S_1}{4}I_1=\frac{vkW}{4}I. \quad . \quad . \quad . \quad . \quad (2)$$

Condition attained in steady state under constant emission E.

From the above equations we find that when the conditions become steady (i. e., $dI/dt=0=dI_1/dt$) the intensities have maximum values given by

$$I_{max.}=\frac{4E}{vaS\left(1-\frac{k^2W^2}{aSa_1S_1}\right)}, \quad . \quad . \quad . \quad . \quad (3)$$

$$I_{1max.}=I_{max.}\left(\frac{kW}{a_1S_1}\right). \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Emission stopped after steady state has been reached.

If through prolonged use of the source E the intensity has reached the steady values given in (3) and (4), and if the source is then suddenly stopped, the subsequent decay of sound (with E=0) is given by the following solutions of the differential equations (1) and (2), viz. :—

$$I=I_{max.}\left\{\frac{1-\frac{4V_1\lambda_1}{va_1S_1}}{1-\frac{\lambda_1}{\lambda_2}}e^{-\lambda_1 t}+\frac{1-\frac{4V_1\lambda_2}{va_1S_1}}{1-\frac{\lambda_2}{\lambda_1}}e^{-\lambda_2 t}\right\}, \quad . \quad (5)^*$$

$$I_1=I_{1max.}\left\{\frac{1}{1-\frac{\lambda_1}{\lambda_2}}e^{-\lambda_1 t}-\frac{1}{\frac{\lambda_2}{\lambda_1}-1}e^{-\lambda_2 t}\right\}, \quad . \quad . \quad (6)$$

* If (5) and (6) be written $I=AI_{max.}$ and $I_1=A_1I_{1max.}$ respectively, then the solution of equations (1) and (2) corresponding to uniform sound emission beginning at zero time is

$$I=I_{max.}(1-A) \text{ and } I_1=I_{1max.}(1-A_1).$$

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where

$$\lambda_1 = \frac{v}{8}\left(\frac{aS}{V} + \frac{a_1S_1}{V_1}\right) - \frac{v}{8}\sqrt{\left(\frac{a_1S_1}{V_1} - \frac{aS}{V}\right)^2 + \frac{4k^2W^2}{VV_1}}, \quad (7)$$

$$\lambda_2 = \frac{v}{8}\left(\frac{aS}{V} + \frac{a_1S_1}{V_1}\right) + \frac{v}{8}\sqrt{\left(\frac{a_1S_1}{V_1} - \frac{aS}{V}\right)^2 + \frac{4k^2W^2}{VV_1}}. \quad (8)$$

These expressions give the general conditions under which reverberant sound dies away in the two rooms when the source is stopped. It remains to ascertain the conditions to be fulfilled in the design of the chambers in order that simpler relations may be obtained.

Conditions for Simpler Formulæ.

(i.) The expressions (7) and (8) defining λ_1 and λ_2 are much simplified if k^2W^2/VV_1 be small compared with $(aS/V - a_1S_1/V_1)^2$.

Since, as we shall see later, V should be larger than V_1, and a_1S_1/V_1 should be several times as great as aS/V, the above condition would be satisfied if, in addition, kW were sufficiently small compared with a_1S_1.

With the condition fulfilled we have the great simplification

$$\lambda_1 = \frac{raS}{4V}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

$$\lambda_2 = \frac{ra_1S_1}{4V_1}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

and equation (5) reduces to $I = I_{max.}e^{-\lambda_1 t}$.

(ii.) Within the brackets of (6) the term remaining in $e^{-\lambda_2 t}$ rapidly becomes negligible compared with that in $e^{-\lambda_1 t}$ provided λ_2 be several times as great as λ_1, *i.e.* if the absorbing power per unit volume for the second chamber (a_1S_1/V_1) be sufficiently great compared with that (aS/V) for the source room. Even a moderate ratio of say 2 or 3 may be sufficient in suitable cases. To this end the second room should be smaller than the first (since area per unit volume is greater for small rooms) and its surface should be more absorbent.

Possibly it is unnecessary to simplify further, but if λ_2 be as much as fifty times as great as λ_1, then the coefficient of $e^{-\lambda_1 t}$ within the brackets of (6) differs from unity by only 2 per cent., an amount which would not be perceptible in ordinary reverberation work. The higher absorptive power necessary for this would be advantageous in damping any tendency for the room to act as a resonator.

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Simplified Formulæ.

With all the conditions fulfilled, the residual intensities in the rooms rapidly attain the values

$$I = I_{\text{max.}}\, e^{-vaSt/4V}, \quad . \quad . \quad . \quad . \quad . \quad (11)$$

$$I_1 = I_{1\,\text{max.}}\, e^{-vaSt/4V}, \quad . \quad . \quad . \quad . \quad . \quad (12)$$

where

$$\frac{I_{\text{max.}}}{I_{1\,\text{max.}}} = \frac{a_1 S_1}{kW}. \quad . \quad . \quad . \quad . \quad . \quad (13)$$

The quantity $(I_{\text{max.}}/I_{1\,\text{max.}})$ may be called the reduction factor for the partition, under the conditions considered.

If now T and T_1 be respectively the times which elapse in the two rooms before the reverberant sound dies away from its initial maximum value to the threshold of audibility, we have

$$I_{\text{max.}}\, e^{-vaST/4V} = I_{\text{min. aud.}} = I_{1\text{max.}}\, e^{-vaST_1/4V}, \quad . \quad . \quad (14)$$

whence

$$\log\left(\frac{a_1 S_1}{kW}\right) = \frac{vaS}{4V}(T - T_1), \quad . \quad . \quad . \quad (15)$$

a simple equation involving k.

The factor $\frac{vaS}{4V}$ determining the rate of decay of the sound can be obtained from a preliminary calibration of the room. For this the duration of reverberation would be determined first with a source of intensity E, and then with another of intensity nE: the difference in duration is the time taken for n-fold decay of sound in the room, and is a measure of $vaS/4V$.

The simplified formulæ given above will not generally apply to the case (presumably $k=1$) of an uncovered aperture, owing to conditions which have been introduced in the analysis. However, on extrapolating a curve of experimental results to which the formulæ apply—say, for a series of diminishing thicknesses of porous non-resonant material—it is towards the value a_1S_1/W_1 that the reduction factor tends as the condition of an uncovered aperture is approached, and not towards unity as might be conjectured at first glance. It is interesting, therefore, that P. E. Sabine *, working with various musical notes, found a reduction factor of about $2\frac{1}{2}$ to be indicated on an average for zero thickness of felt. While he suggests that this result may be due to surface phenomena in transmission by

* P. E. Sabine, 'Am. Architect,' Sept. 28, 1921.

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felt, the above analysis indicates that, apart from such a cause, factors greater than unity may arise from the circumstances of the experiment.

Audibility at special points in the second room.

In some conditions the above equations for reverberant sound may not represent the sound actually heard at a given point in the second room. For instance, if the room were very large and completely absorbent, there would be no general reverberation within it, but an ear situated close to the partition would detect transmitted sound. An estimate may be made of the intensity in this case. According to the above considerations, the energy transmitted in unit time through unit area of the partition would be $\frac{1}{4}kv\mathrm{I}$, which, in a simple progressive wave, corresponds to an intensity of $\frac{1}{4}k\mathrm{I}$ energy units per unit volume. With the sound in the source room decaying exponentially according to equation (11), the intensity of the entrant sound just near the partition would be

$$\mathrm{I}_e = \tfrac{1}{4}k\mathrm{I}_{\mathrm{max.}}e^{-vaSt/4V}, \quad . \quad . \quad . \quad . \quad . \quad (16)$$

a quantity which differs from the reverberant sound of equation (12) in the ratio $\frac{1}{4} : \mathrm{W}/a_1\mathrm{S}_1$.

Consequently, in some circumstances, it may depend upon the position of the hearer whether (12) or (16) more nearly represents the audibility observed in the second room. However, if the chamber be suitably designed, both entrant and reverberant sound should die away at the same rate as that in the source room, and reduction factors obtained should bear a simple relation to k. The actual relation in a given case should be the subject of experiment.

Summary.

The subject of the paper is related to a method of measuring the transmission of sound through partitions. Equations have been derived for the decay of reverberant sound in each of two chambers connected by an incompletely soundproof partition, when a source in one of the chambers is suddenly stopped. While in general the relations are complicated, they are considerably simplified if the receiving chamber has adequate absorbing power compared with the transmitting power of the partition, and if it is sufficiently less reverberant than the source room.

March 1925.

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VII. *The Theory of the "Schrot-effect."* By NORMAN CAMPBELL, *Sc.D.**

SUMMARY.—Attention is drawn to a general proposition relating the fluctuations in any fortuitous phenomenon and those in an instrument by which it is observed. Use of it would avoid the elaborate calculations upon which the study of the schrot effect has been based hitherto, and enable the observations to be interpreted much more directly in terms of measurements.

The results obtained by Hull and Williams with secondary emission are discussed; it is shown that conclusions other than those that they draw are not excluded.

1. IN the course of a study of the discontinuity of photoelectric emission †, a general proposition was established which is valid in the study of discontinuous processes of any other kind, and, in particular, in the study of Schottky's ‡ "schrot" effect, or the discontinuity of thermionic emission. It was shown that if $\overline{x^2}$ is the mean square deviation from the average of the number of events occurring in unit time; if

$$\theta = f(t) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

gives the reading of an indicating instrument at time t after the occurrence of one of these events at $t=0$, this event being followed by no others; and if $\overline{\theta^2}$ is the mean square deviation of θ from its mean, when the events are occurring in their normal fortuitous succession, then

$$\overline{\theta^2} = \overline{x^2} \int_0^\infty f^2(t)\,dt. \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The only limitations imposed upon the function f are that $f(\infty)$ should be zero, and that the effects of successive events on the instrument should be strictly additive.

Fürth § has, in effect, used this proposition to calculate the schrot effect, when the observing instrument is assumed to be an ideal damped harmonic oscillator attached to

* Communicated by the Author.

† N. R. Campbell, Proc. Camb. Phil. Soc. xv. pp. 117, 310, 513 (1909–1910).

‡ W. Schottky, *Ann. d. Phys.* lvii. p. 541 (1918).

§ R. Fürth, *Phys. Zeit.* xxiii. p. 354 (1922).

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amplifiers giving the same amplification for all kinds of disturbances. He attempted no formal proof of it; and Fry *, in his discussion of all attempts to calculate the schrot effect, dismisses it summarily as based on a mere analogy. I would urge, on the contrary, that it is the only formula yet offered which is based by unexceptionable logic on physical assumptions that can be disentangled from the argument and discussed separately.

The most important of these assumptions is that the effects of isolated electrons on the observing system are strictly additive, even when their passages through it are separated by intervals comparable with its period. Fry insists on the importance of this assumption, and, indeed, it is almost obvious that no observing instrument can measure truly the schrot effect, which depends on the isolation of the electrons, unless it is true. And yet it might well be doubted; it might be thought, for example, that when a single isolated electron passed through a system, there could be no quantity such as self-induction †. Schottky's treatment of the problem by means of Fourier analysis conceals the assumption; it is very difficult to discover at what point of the argument it is introduced. It may be urged, therefore, that the only evidence in favour of the result that Schottky reached by exceedingly involved analysis is that it is the same as that reached by Fürth, on the basis of (2), by the simplest algebra.

2. Hull and Williams ‡ object to Fürth's formula that it does not cover the case of their apparatus, because they find that the amplification is not entirely independent of the frequency of a harmonic disturbance. Their contention is, of course, true; but their method of avoiding the difficulty is open to grave objection. They revert to Schottky's Fourier analysis, but introduce an empirically determined amplification factor, varying with the frequency of the components. It is never satisfactory to introduce an empirical correction into a theory which does not show explicitly the need for it; there is always the danger of assuming in the theory propositions which are effectively denied in making the correction. This danger is present here. The variation of the amplification factor may well be due to a variation of the inductances and capacities with the frequency. But if the inductances and capacities in the amplifiers vary with the frequency, is it certain that those in the oscillating circuit, excited by the

* T. C. Fry, Journ. Frank. Inst. cxcix. p. 203 (1925).
† *Cf.* N. R. Campbell, 'Modern Electrical Theory,' 2nd ed. p. 129.
‡ A. W. Hull and N. H. Williams, Phys. Rev. xxv. p. 148 (1925).

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thermionic discontinuities, are independent of the frequency, as the theory assumes? There is no doubt that their formula is very nearly right; the correction is small, and it must be in the right direction. But when they claim that their method might give a value for the electronic charge more accurate than that obtainable by any other method, they appear to forget that their greater experimental accuracy is set off by greater theoretical uncertainty.

It may be worth while, therefore, to point out that all this difficult and obscure calculation could be avoided, ideally if not actually, by a direct experimental determination of $\int_0^\infty f^2(t)$ in (2). For this purpose, a known charge Q_1, so small that it lies within the additive range, is passed from cathode to anode of the thermionic tube in a time short compared with the period of the oscillating circuit; the total charge Q_2 passing through the rectifier in consequence is measured. If the rectifier obeys accurately the "square law,"

$$Q_2 = \int_0^\infty I\,dt = \int_0^\infty \alpha V^2\,dt, \quad . \quad . \quad . \quad . \quad (3)$$

where I is the current through the rectifier associated with a voltage V across its terminals. Q_2 should be proportional to Q_1^2; if it proves to be so, and if we identify θ in (2) with V, we shall have

$$\overline{V^2} = \overline{x^2} \cdot \frac{\epsilon^2}{Q_1^2} \int_0^\infty V^2\,dt. \quad . \quad . \quad . \quad . \quad . \quad (4)$$

But

$$\overline{x^2} = i_0/\epsilon, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where i_0 is the mean thermionic current. Hence, if $\overline{I}$ is the mean current through the rectifier,

$$\overline{I} = \alpha\overline{V^2} = \frac{i_0}{\epsilon} \cdot \frac{\epsilon^2}{Q_1^2} \cdot Q_2, \quad . \quad . \quad . \quad . \quad . \quad (6)$$

or

$$\epsilon = \frac{\overline{I}}{i_0} \cdot \frac{Q_1^2}{Q_2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

If, as in Hull and Williams's experiments, the frequency of the oscillating circuit is of the order of one million, there would be great difficulty in securing the passage of Q_1 in a time short compared with the period; but if low-frequency circuits were used, there would be no difficulty. The problem

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of determining $\bar{I}$ can then be solved simply enough by taking a sufficient number of readings, if necessary by a recording instrument, and averaging them arithmetically.

3. However, the experiment would hardly be worth the labour expended on it. It is unlikely that the accuracy of Millikan's determination of ϵ could be approached; and, on the other hand, the work of Hull and Williams and others has established that the quantities observed are measures of the thermionic fluctuations, although the unit of measurement may be slightly uncertain. The value of such experiments will probably lie now in comparative, and not absolute, measures of the schrot effect, such as those already made on the effect of the space-charge and of secondary emission.

But it may not always be easy to interpret the results. Thus Hull and Williams, having shown that the fluctuations from their insulated plate are the sum of those due to the primary and secondary electrons, conclude that the emission of the secondaries is entirely "independent" of the primaries. By this they seem to mean that the emission of a secondary must be entirely uncorrelated with that of the primary, and may occur at any instant after the incidence of the primary. But that conclusion is not really established so far by their experiments. There might be fluctuations even if the emission of the secondary was simultaneous with the incidence of the primary or always followed it at an interval short compared with the period of the oscillating circuit. For it is consonant with what is known of secondary emission to suppose that the number of secondaries emitted by the incidence of a single primary varies about a mean; the fluctuations of this number would produce a schrot effect.

The problem is very similar to one discussed in connexion with photoelectric emission*. Let the mean number of secondaries emitted by one primary be ω, and let η represent the variations of the number about this mean. Then if N is the mean number of primaries striking the plate per unit time, and ξ the variation of this number from the mean during a very short time τ, then the gain of electrons by the plate during τ is

$$(N\tau+\xi)-(N\tau+\xi)(\omega+\eta), \quad . \quad . \quad . \quad (8)$$

and the value of $\overline{x^2}$ in (2) is given by

$$\overline{x^2}=N\{(1-\omega)^2+\overline{\eta^2}\}. \quad . \quad . \quad . \quad . \quad . \quad (9)$$

* Campbell, *loc. cit.* p. 314.

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Here it is assumed that the emission of the secondaries is simultaneous with the incidence of the primary; if emission and incidence are independent in Hull and Williams's sense, then in place of (8) we have

$$(N\tau+\xi_1)-(N\tau+\xi_2)(\omega+\eta), \quad . \quad . \quad . \quad (10)$$

ξ_1 and ξ_2 being independent with the same mean values, and in place of (9)

$$\overline{x^2}=N\{1+\omega^2+\overline{\eta^2}\}. \quad . \quad . \quad . \quad . \quad (11)$$

In this calculation it is assumed that, within any interval τ, however short, a primary is as likely to be incident at any one instant as at any other. If the fluctuations of the primaries are partly suppressed by a space-charge, and electrons tend to follow each other at regular intervals, the argument breaks down. At the other extreme, when the intervals are perfectly regular, it is easy to show that in place of (9) we have

$$\overline{x^2}=N\overline{\eta^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

and in place of (11)

$$\overline{x^2}=N(\omega^2+\overline{\eta^2}). \quad . \quad . \quad . \quad . \quad . \quad (13)$$

The intermediate case, which is that of Hull and Williams, when the regularity is partial, cannot be treated accurately without a precise knowledge of the form of regularity; but it seems reasonable on all accounts to assume that if the regularity introduced by the space-charge is such as to reduce the fluctuations in the primaries in the ratio β, then we shall have in place of (9)

$$\overline{x^2}=N\{\beta(1-\omega)^2+\overline{\eta^2}\}, \quad . \quad . \quad . \quad . \quad (14)$$

and in place of (11)

$$\overline{x^2}=N\{\beta+\omega^2+\overline{\eta^2}\}. \quad . \quad . \quad . \quad . \quad . \quad (15)$$

In Hull and Williams's experiments ω was 1; their experimental result was

$$\overline{x^2}=N\{\beta+\omega^2\}.$$

If that result is general for all values of ω—that is to say, for all ratios of primary to secondary current, and therefore for all energies of the primaries,—then their conclusion truly follows, and with it the conclusion that $\overline{\eta^2}=0$. But it is so surprising to find that, while there is complete temporal independence between emission and incidence, the number of secondaries emitted by each primary is not subject to

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appreciable variations, that it is to be hoped that they will extend their observations over a wider range. A single experiment, in which $\omega=1$, cannot distinguish between (14) with $\overline{\eta^2}$ fortuitously equal to $1+\beta$ and (15) with $\overline{\eta^2}=0$; or, further, between either of these alternatives and some relation intermediate between (14) and (15) with some intermediate value η^2, corresponding to partial but not complete temporal independence.

VIII. *A Study of the Electrolytic Interrupter.* By J. A. Crowther, *Sc.D., F.Inst.P., Professor of Physics, University College, Reading, and* R. J. Stephenson, *B.Sc.**

[Plate II.]

Introduction.

THE Wehnelt electrolytic interrupter is from a mechanical point of view one of the simplest interrupters for use with an induction coil, and still provides one of the most effective methods of producing continuous interruptions of really large currents. It consists essentially of a metal wire (usually platinum) projecting through a small hole in a non-conducting cylinder into an electrolytic solution. This "point," as it is called, serves as the anode; the cathode is a large plate of lead or some other indifferent metal dipping in the same solution. Sulphuric acid at its maximum conductivity is the electrolyte usually employed, but similar effects are produced in other electrolytes, and ammonium phosphate is now often used as it does not evolve noxious fumes. If the current to be interrupted is very large, three or more points connected in parallel and dipping into the same vessel can be employed.

The principal characteristics of the break in use are as follows:—(*a*) The interruptions of the current are very sharp. This is shown by introducing an oscillograph into the current circuit (see Pl. II. fig. 6 *a*). The sharpness of the breaks is quite comparable with that of a mechanical interrupter. (*b*) The interruptions are very regular. The break when working normally emits a note, which, though hardly to be described as musical, is of very definite and perfectly recognizable pitch. The pitch of the note depends on the length of point exposed, on the supply voltage, and

* Communicated by the Authors.

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on the resistance and self-induction of the circuit, and in certain conditions is very sensitive to quite small changes in resistance and induction. (*c*) The point, when the break is working, is covered with a bluish glow. Examination with a revolving mirror showed that this glow was actually intermittent. In order to determine at what part of the current cycle this glow occurred, an image of the point was focussed upon a falling photographic plate upon which a current oscillograph in series with the break registered its deflexions. The resulting photograph (Pl. II. fig. 1) shows that the luminosity corresponds to the break in the current, and apparently takes place at the moment when the current is about to be re-made. The sharpness of the image of the point indicates that the flash is practically instantaneous. There is no perceptible drawing-out of the image, although the plate was falling with an average speed of 1 metre per second. (*d*) Finally, when two or more points are connected in parallel, interruption takes place simultaneously at all the points, and no particular care in adjustment is required to produce this effect.

The behaviour of the break is generally ascribed to the temporary formation of a non-conducting layer round the point by the collection of the gas bubbles which are produced there by the electrolysis. It seemed to us, however, that some further phenomenon must be involved to account both for the extreme sharpness and the regularity of the interruptions. Experiments were therefore made to investigate the action of the break in more detail. After a considerable number of oscillograms, both of the current through the break and of the potential difference across it, had been taken and examined, a clue to the action was finally discovered in the nature of the current-voltage curves for conduction through an unsymmetrical electrolytic cell, such as the Wehnelt break supplies. It will be convenient to discuss these curves before dealing with the oscillograms.

Current-voltage Curves for conduction through an Electrolyte with a Point Anode.

The apparatus employed was of the simplest. The wire forming the anode protruded through a hole in the bottom of a pyrex glass tube which was drawn down to fit it as closely as possible. This dipped into a beaker containing the electrolyte, and a plate of lead dipping in the same beaker formed the negative pole. This simple arrangement performed all the functions of a Wehnelt interrupter when the circuit included a suitable inductance. In the experi-

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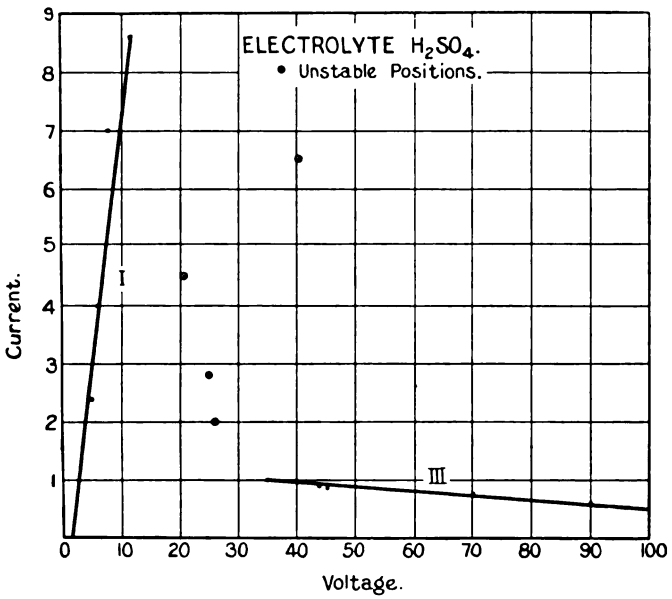
ments described in this section, however, as the effect of resistance only was to be investigated the circuit was non-inductive, the voltage being supplied by a large battery of accumulators. The current was measured by an ammeter in series with the break, and the voltage by a high-resistance voltmeter connected across its terminals.

Fig. 2.



Current-voltage curve for sulphuric acid.

Fig. 2 is typical of the kind of results obtained. It was obtained using a platinum point 1·0 cm. in length and ½ mm. in diameter in dilute sulphuric acid of S.G. 1·20. It will be seen that the curve falls into three sections. In the first part of the curve we have the normal relation between current and voltage for an electrolytic conductor. The current begins to flow when the applied voltage exceeds the polarization E.M.F. and increases linearly with the voltage until the voltage across the break is 12·5 volts. The corresponding current in this particular instance was 8·7 amperes, and this was the maximum current which could be passed through this particular system. If the voltage was increased beyond this point the average current, as measured by the ammeter, became smaller. At the same

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time, both the voltmeter and ammeter began to show very considerable fluctuations, which made accurate readings impossible. This stage lasted until the applied voltage was rather more than 30 volts, when conditions again became steady, the current for a P.D. of 35 volts being 1·0 ampere. If the voltage was now still further increased, the current became progressively smaller and decreased almost linearly with increase in voltage. This is indicated by the straight line between 35 and 100 volts on the graph. It may be mentioned that the point was usually non-luminous throughout this range of voltages.

A repetition of the experiments with the same electrolyte, but with different anode points, gave exactly similar graphs. It was found that for the same electrolyte the critical voltage at which the change in the graph occurred (12·5 volts in the case of sulphuric acid) remained the same. Thus doubling the length of the point or doubling its diameter gave in each case a graph showing a discontinuity at exactly the same voltage. The corresponding current at this voltage, however, increased with the area of wire exposed, and was found to be directly proportional to it. Hence we may also express the results of these experiments by saying that the current ceased to be proportional to the P.D. when the current density at the point reached a value which was a constant for a given electrolyte. For sulphuric acid of the strength named, its value was about 45 amperes per sq. cm. Reasons will be given later which suggest that the P.D. is the more fundamental factor.

Analogous results were obtained with a number of other electrolytes, including sodium hydrate, sodium chloride, sodium sulphate, hydriodic acid, and ammonium phosphate. The critical voltage differed with the electrolyte. For sodium hydrate it was 24 volts, and for ammonium phosphate somewhere in the neighbourhood of 45 volts. It appeared to vary slightly with the strength of the solution. The phenomena for ammonium phosphate were not quite so well marked as for the other electrolytes used. The intermediate stage extended over a longer range of voltages, and the final stage in which the current decreased regularly with increase in voltage did not become established for potential differences less than 90 volts. The conductivity of the break in this stage was also greater than when sulphuric acid was employed, although the normal conductivity in the first stage was much smaller. A current-voltage curve for ammonium phosphate is shown in fig. 3. It will be seen that it does not differ essentially from that for sulphuric acid.

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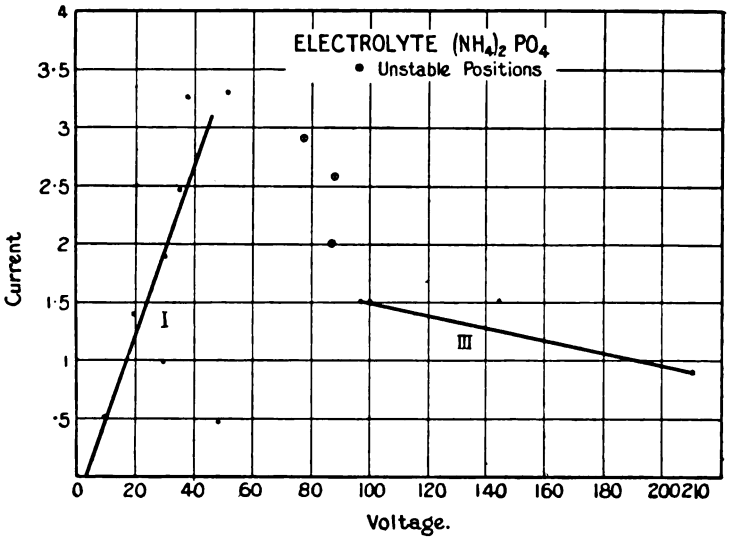
Experiments made with points of other metals, including iron, nickel, and lead, gave precisely similar results. The critical voltage appeared to be slightly less with these elements than with platinum (11 volts in dilute sulphuric

Fig. 3.



Current-voltage curve for ammonium phosphate.

acid as against 12·5), but the phenomena were otherwise the same. Unfortunately, all these metals disintegrate rapidly in use, and they cannot, therefore, be used as substitutes for platinum in the Wehnelt break.

Phenomena at the Point.

An examination of the point during the experiments just described revealed very interesting changes in the method of evolution of gas in the different stages into which the conduction falls. In the normal stage the gas was given off from all parts of the point in bubbles of moderate size, such as generally attend the evolution of gas by electrolysis. Pl. II. fig. 4 *a* is a photograph of the point in this stage. The actual appearance to the eye is that of a rapid stream of bubbles rising rapidly to the surface, but as the time of exposure was 1/200 of a second, only a few of these bubbles appear in the photograph. On increasing the voltage so as

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to bring in the third stage, the appearance of the point was entirely altered. Instead of leaving the wire in bubbles, the gas evolved seemed to cling to it tenaciously, gradually working its way upwards until it reached the glass sheath, where it collected into a single bubble of considerable size, which broke away from time to time. This is indicated by the photograph in Pl. II. fig. 4*b*. The way in which the little bulges to be seen in the photograph gradually worked their way up the wire was very characteristic, and conveyed strongly the impression that the gas was forcing its way up inside a tightly-fitting elastic skin enclosing the wire. This impression may be quite erroneous as an explanation of the effect, but it is certainly a very close description of it.

In the intermediate stage the gas was evolved partly in the form of the bubbles characteristic of the first stage, and partly in the form of large bubbles from the point characteristic of the third stage. The most striking feature of this stage, however, was the formation of large numbers of very minute bubbles which were shot off from the point with considerable velocities, so that, in a short time, the whole of the liquid became quite milky in appearance. The bubbles were so minute that this milkiness took some minutes to clear.

The second stage thus appears to be a series of rapid alternations between the first and third stages. The transition could actually be watched in the case of ammonium phosphate when the applied voltage was just below that required to ensure permanence for the third stage. The silvery film on the point would break down every now and then, its dissolution being signalized by a spurt of very minute bubbles and a simultaneous kick of the ammeter needle. This suggestion is amply confirmed by oscillographic records of the current in the three stages. Pl. II. fig. 5*a* (with ammonium phosphate in the interrupter) was taken with an applied voltage of 42 volts (just below the critical voltage for the electrolyte), while Pl. II. fig. 5*b* shows the same circuit with the P.D. across the break increased to 46 volts. The fluctuations, shown in the latter oscillogram, were found to increase in amplitude and frequency as the voltage was further increased, until finally, at sufficiently high voltages, the current again became steady at a much lower value.

It may be mentioned in passing that, with sulphuric acid as the electrolyte, the gas given off during the transition stage was strongly ozonized; the large bubbles emitted during the third stage smelt strongly of oxides of sulphur, and at high voltage were sometimes filled with white fumes.

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Application of the Results to the Action of the Interrupter.

The current-voltage graphs described in a previous section were obtained by adjusting the voltage in circuit to the required value by altering the number of accumulators employed. The voltage across the break can also be adjusted by having a variable resistance in series with the break. The actual P.D. across the break is then the difference between the applied voltage and the product of the external resistance into the current. Suppose now we apply 100 volts to a circuit containing a variable resistance and the Wehnelt break, the current-voltage curve for which is indicated in fig. 2. Starting with a high resistance and consequently a small voltage across the break, we can, by gradually reducing the resistance, describe the first portion of the curve. As soon, however, as the P.D. across the break exceeds 12·5 volts the current begins to fluctuate, owing to momentary passages into the third stage. As the current falls, the drop of potential in the external resistance becomes less and the voltage across the break becomes greater. This greater voltage still further reduces the current, owing to the nature of the graph. The system is thus unstable, and jumps across the intermediate stage to the third stage. The voltmeter thus moves, with a jump, from the critical voltage to a voltage only slightly less than the full voltage in the circuit. This is very easily verified by experiment.

If, now, inductance is included in the circuit instead of resistance, a somewhat similar state of affairs is produced. When the voltage across the break has risen to a value greater than the critical value, fluctuations in the current begin. As the current begins to fall, an E.M.F. is induced in the circuit, producing a rapid increase in the applied voltage across the interrupter, and thus throwing it into the third or highly resistant stage. The current thus falls with great rapidity from its maximum value (8·7 amperes in the case illustrated in fig. 2) to the value corresponding to this higher voltage. If the inductance is very small, the induced voltage may not be sufficient to throw the system into the third or highly resistant stage, and the effect will simply be to emphasize the fluctuations in the current. This is shown by the oscillogram in Pl. II. fig. 5 *c*, where the conditions were identical with those for Pl. II. fig. 5 *b*, except that a small inductance (0·1 millihenry) was included in the circuit without altering the total resistance.

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If the self inductance is larger, the induced E.M.F. will be sufficient to throw the system into the highly resistant stage, and the current will fall rapidly to half an ampere or less. This rapid change in current will produce a still higher induced E.M.F. in the circuit, an E.M.F., in fact, sufficiently high to spark through the resistant layer and destroy it.

The cycle of operations in the Wehnelt break is thus as follows :—When the circuit is made, the voltage across the break gradually rises until, after a time depending on the time constant of the circuit, it reaches a value exceeding the critical value. The current then begins to fall rapidly, and an induced E.M.F. is produced which rapidly attains the sparking voltage, while the current falls to a small value. A discharge then takes place across the resistant layer, thus destroying it and bringing the system back to the normal stage. The current then begins to rise again, and the cycle is repeated indefinitely. The luminous discharge thus takes place during the break, as indicated in Pl. II. fig. 1, and its function is to restore the system to its conducting phase.

It will be seen that the principal characteristics of the interrupter become immediately explicable on this view of the phenomenon. The sharpness of the interruptions is due to the sudden change in resistance of the break when the conduction passes from one phase to the other. The regularity of the interruptions is also explained, since the time which it takes for the voltage across the break to rise to a definite value will be determined by the applied voltage and the time constant for the circuit, *i.e.* by its resistance and self inductance (and possibly its capacity), and will be a constant for a given circuit. The simultaneous working of two or more points in parallel is also accounted for, since the potentials of all the points must be the same, and all will reach the critical condition at the same time.

Evidence from the Oscillographic Records of Current and Voltage.

The theory suggested in the previous section was amply corroborated by oscillographic records made of the behaviour of the interrupter under varied working conditions. Oscillograms of the current through the break were made by a simple high-frequency-current oscillograph of the Duddell type connected across the terminals of a low resistance in series with the break. Those of the P.D. across the break

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were obtained by connecting the same current oscillograph across the terminals of the break through a high resistance (2000 ohms and upwards). The inductances placed in series with the break were the various layers of the primary of a large induction coil. The secondary of the induction coil was removed during these experiments, in order to avoid the complications which might arise owing to the reaction of the secondary circuit on the primary. These reactions probably play an important part in determining the efficiency of the interrupter as part of an X-ray outfit, and we hope to investigate this part of the problem later. In discussing the theory of the interrupter itself, it seemed desirable to keep the conditions of the circuit as simple as possible.

Typical oscillograms of current and voltage are reproduced in Pl. II. fig. 6 *a* & *b*. The sudden fall in current and the corresponding rise in the P.D. are clearly shown. The maximum potential reached is far too high to be recorded on the scale of Pl. II. fig. 6 *b*. By increasing the resistance in circuit with the potential oscillograph to 10,000 ohms, the complete potential curve could be obtained, and an example is reproduced in Pl. II. fig. 6 *c*. The peak potential as calculated from the calibration curves for the oscillograph was 600 volts in this particular case, and in general varied between 400 and 600 volts. These values are of the order of the minimum sparking voltage in oxygen, and direct experiment showed that a luminous discharge was actually produced at the point when a steady P.D. of 420 volts was applied directly across the interrupter in the absence of self induction.

The hypothesis that the interruption in the current occurs when the P.D. across the break reaches a definite value, which depends only on the electrolyte, can be verified directly from the potential oscillograms. A series of such oscillograms was taken in which all the conditions in the circuit were varied except the electrolyte. Experiments were made with applied voltages varying from 68 volts to 210 volts, with and without external resistance in circuit; with a variety of self inductances; and with points of various lengths and diameters. The critical breaking voltage to be measured was taken as that corresponding to the point on the potential graph where the voltage takes a sharp upward turn, and this discontinuity was generally sufficiently marked to be measured with reasonable accuracy. This voltage was found to be, within the limits of experimental error, quite independent of the changes made in the circuit. With

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sulphuric acid of S.G. 1·20 as the electrolyte, all the measurements lay between 24 volts and 26 volts, and these slight variations appeared to be quite accidental.

A comparison with the current-voltage graph for the electrolyte suggests that this voltage marks the point at which the third stage of conduction sets in. This, we suggest, is what might be expected, as the irregular transitions which characterize what we have called the intermediate stage usually take some little time before they manifest themselves (see Pl. II. fig. 5), and with a rapidly rising voltage, such as we have in these experiments, the probability that such an interchange will occur before the voltage has reached that at which the third stage is definitely established is very small.

The conduction, until the moment of break, is in the normal stage, and the peak value of the current, as read from the oscillograms, is much higher than the maximum steady current which can be sent through the break. In fact it corresponds to the value of the current which would be obtained by producing the first straight portion of the current-voltage curve for the interrupter to the measured breaking voltage. This explains an observation which often puzzled us in the earlier stages of the work, that the average current through the break as measured by an ammeter was very materially increased when self induction was introduced into the circuit. By instantaneous measurements, therefore, it appears possible to prolong each of the straight portions of the current-voltage curve to a common voltage, about 25 volts for sulphuric acid, where the real discontinuity occurs, both phases being unstable for a certain range of voltages on each side of this point.

It is possible, however, to produce interruptions in the current when the voltage across the interrupter only slightly exceeds what we have called in the earlier sections of the paper the critical voltage. The production of such interruptions has already been discussed. They are very slow and comparatively irregular. Oscillograms show that in these cases the current rises to a maximum and then remains practically steady. The P.D., however, gradually increases until the usual breaking voltage is reached, when an interruption takes place. This gradual increase in voltage may be due to a gradual increase in resistance of the electrolyte near the point, owing to the rapid removal of the ions by the current. The value of the current at break for these slow interruptions is always appreciably smaller

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than for the rapid interruptions obtained with the higher voltages. It is for this reason that we have suggested that the P.D. rather than the current density is the more fundamental factor in determining the break.

Conclusion.

In the absence of any theory to account for the high resistance developed at the point, we have judged it desirable to record our experimental results without any adjustments or corrections. It may be pointed out that the voltages measured were those across the terminals of the interrupter, whereas in all probability the deciding factor is the fall of potential between the point anode and some point in the electrolyte close to it. Since there is always some current flowing in the interrupter, this will be less than the P.D. between the terminals by the P.D. required to drive this current through the remainder of the electrolyte, which in turn depends on its specific resistance. It is possible that the observed differences between different electrolytes and, in particular, the differences observed between different solutions of the same electrolyte may be due in part to this cause. The fact that the critical voltage increased with the resistance of the electrolyte gives some support to this suggestion.

Until further evidence has been accumulated, it does not seem desirable to advance any suggestions as to the cause of the sudden increase of resistance which occurs when the critical voltage is passed, and which accounts for the action of the Wehnelt interrupter. It is natural to postulate the formation of a highly resistant layer at the anode, and the tightly-clinging gas layer which is so characteristic of this high-resistance stage of the conduction presents itself as a very obvious explanation. The change in the mode of emission of the gas has, however, itself to be accounted for. It is hoped that further experiments may throw some light on this interesting problem.

University College,
Reading,
March 18th, 1925.

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IX. *On an Experimental Verification of Castigliano's Principle of Least Work and of a Theorem relating to the Torsion of a Tubular Framework.* By Professor A. J. SUTTON PIPPARD, *M.B.E., D.Sc., University College, Cardiff, and* J. F. BAKER, *B.A.**

THE mathematical proof of the "Principle of Least Work" was given in Castigliano's original treatise †, and recently Mr. R. V. Southwell has demonstrated the physical basis of the theory ‡.

During the past year the present authors have carried out experimental work upon the properties of certain braced frameworks, and in the course of these experiments very satisfactory verification of the Principle was obtained. Although the truth of the Principle has been established by the work cited, the importance of the method and its wide range of application makes experimental evidence of some interest and value, more particularly since very little experimental work of any kind upon braced frameworks appears to have been published.

In addition to the verification of Castigliano's Principle, experiments were made to check a theorem relating to the stress distribution in a tubular framework subjected to torsion. This theorem, due originally to Batho §, has recently been obtained independently by Southwell ‖ in an investigation of the case of tubular frameworks with redundant bracing members. The work upon which the authors were engaged was of a more comprehensive character than outlined above, and is fully described elsewhere ¶, but since much of it was of a specialized interest, only those experiments bearing on the two theorems mentioned are included here.

The framework upon which the experiments were conducted was a space frame in the form of a braced hexagonal tube consisting of six longitudinal members divided into a number of equal bays by transverse frames in the form of regular hexagons: the panels thus formed by the transverse strut members and the longitudinal members were braced across both diagonals (figs. 1 and 2).

* Communicated by Mr. R. V. Southwell, M.A.

† 'Elastic Stresses in Structures'—English translation by E. S. Andrews, 1919.

‡ Phil. Mag. Jan. 1923.

§ 'Engineering,' Oct. 15, 1915, p. 398.

‖ Aeronautical Research Committee, R. & M. 791.

¶ Aeronautical Research Committee. R. & M. 948.

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The theoretical stress analysis for such a framework supported at one end and loaded at the other has been fully worked out * upon the following assumptions :—

(1) The framework was assumed to be pin-jointed throughout.

(2) The transverse framework to which the load was applied was assumed to be rigid in its own plane but free to warp out of that plane.

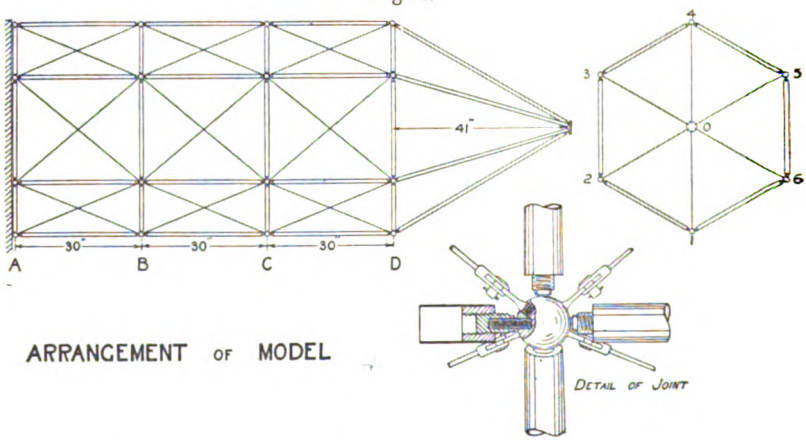
(3) All members were assumed capable of resisting either tensile or compressive forces.

(4) All longitudinal members were assumed to be of the same size except the bottom or "keel" member which could be made any desired area.

Description of Structure.

The leading dimensions of the experimental structure and some details of its construction are shown in fig. 1. The

Fig. 1.



framework was 3 bays in length, each bay being 30 inches long ; the side of the hexagon was 25 inches. Since the theoretical analysis had been based on the assumption that the structure was pin-jointed throughout, an attempt was made to design a suitable joint of this type. The difficulties in this will be apparent, and although several designs were made it was found that even in the best of them the friction on the bearing surfaces would have been considerable, and would

* Aeronautical Research Committee, R. & M. 800, Appendix V.

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in fact have introduced a fixing factor of an incalculable amount. The attempt to obtain true pin or ball ends was therefore abandoned, and a suggestion made by Mr. R. V. Southwell was examined: this suggestion was that the members of the structure should be attached to the joints by short dowels or pins, which would be of sufficient cross sectional area to transmit the direct loads in the members, but so short that no tendency to buckle would occur. The necessary strength was given by dowels of small diameter and flexural rigidity: consequently the amount of bending which could be transmitted by them was small, and moreover could be calculated if necessary and allowed for as a correcting factor.

Tests were carried out upon struts with ball ends and with ends fixed by dowels, and the results were such as to justify the latter method of construction. The transverse and longitudinal members of the structure were made of steel tube $\frac{7}{8}$ in. outside diameter and ·028 in. thick. All cross bracing members were 4 B.A. swaged rods, ability to resist compression being obtained by initially tensioning these rods to such an extent that they remained operative under the maximum loads imposed. Provision was made for replacing the keel member by solid steel bars $\frac{7}{8}$ in. diameter, since it was desired to carry out experiments upon the effect of varying the size of this member. The nose-piece of tubes in the form of a regular pyramid, seen in the photograph of the structure (fig. 2), was provided for a special experiment not described in the present paper.

The structure was attached to wall-plates by dowels of the same size as used in the joints, and was loaded at the free end by means of a beam weighing machine, one pan of which was replaced by a special hook fastened to the top joint of the structure, a turn-buckle being inserted between the beam and the joint for adjustment.

Measurement of Strains.

Means for measuring the strains in all the members of the structure to a high degree of accuracy were essential, and for this purpose none of the standard types of extensometer were suitable, either on the score of weight or expense; in consequence, a special instrument had to be designed, and this was done in collaboration with the Cambridge Instrument Company Limited.

Gauges made of thin aluminium, corrugated for the sake of stiffness, were attached to each member of the structure

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by a hardened steel knife-edge and small setscrew; at the end of the gauge was a small circle of glass marked on the

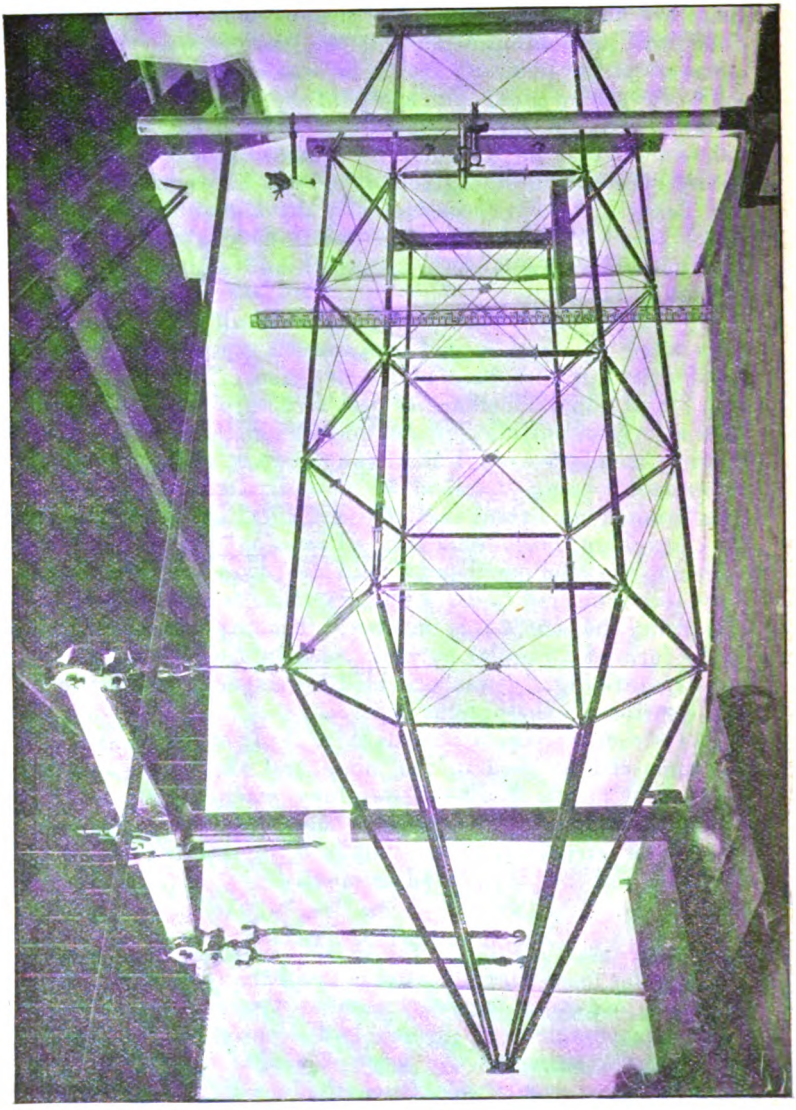

Fig. 2.

under side with two fine cross-lines. The glass was held in contact with the member by small indiarubber bands. A fine line was scratched on the surface of the member by

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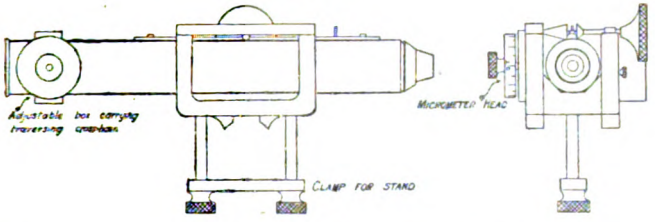
means of a Gillette safety-razor blade, to coincide as nearly as possible with the line on the glass. This was effected by the use of a special marking-off gauge. The distance between the scratches on the member and the glass was measured by a special microscope, and the alteration in this distance under different conditions of loading gave the strain. The gauges were 15 inches between the point of attachment to the member and the line on the glass.

The microscope used is shown diagrammatically in fig. 3. The optical arrangement is standard and needs no special description. The eyepiece is provided with a traversing cross-hair operated by a micrometer head. This cross-hair was first brought into coincidence with the line on the glass and then traversed until it coincided with the scratch on the

Fig. 3.



MICROMETER MICROSCOPE

member. The readings of the micrometer head were noted in each case, and the difference gave the distance between the scratches.

The same procedure was followed after the structure had been loaded, and the difference between the distances before and after loading was the strain produced by the external load system. The movement of the traversing cross-hair as measured by a standard grid was 1/17780 inch per division on the micrometer head, but actual calibration curves were used to reduce the micrometer-head readings to loads in the member, as will be described later.

The objective of the microscope was 2/3 inch, this being the smallest with which reasonable illumination could be obtained under the conditions in which the instrument was to be used. Illumination was obtained from a small 6 volt lamp carried on the end of the microscope; this ensured that the light was always in the same relative position to the scratches which were being viewed through the microscope, and thus error due to variation of the angle from which the light fell was avoided. Since the microscope had to be used on

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all members of the structure in turn it was carried on a steel tubular stand, 2 inches diameter, mounted on a heavy tripod base. This stand was 7 feet high, and the microscope could be attached to any part of it. A tubular extension arm at right angles to the vertical post enabled the instrument to be placed in position for measurements upon the top and bottom members of the framework. The instrument on its stand but without the extension arm is shown on the right of fig. 2, which also shows the gauges in position upon the structure, ready for observation.

By calibrating a tube and a rod under controlled conditions of loading, it was found that with a 15-inch gauge length, one division of the micrometer head was a measure of the strain produced by a load of 7·84 lb. on the tube, and of 1·02 lb. on the rod.

The Conduct of Experiments.

The structure having been erected and trued up, the wires were tensioned so that they could operate as struts. The magnitude of these initial tensions was immaterial as long as they were sufficient to ensure effective strut action under the maximum load to be imposed. An initial load was first placed on the scale-pan and the readings of the gauges taken. The desired increment of load was then applied and the readings again taken. The difference was then reduced to loads by the use of the calibration figures. It was originally intended to mount gauges on all members of the structure and take readings on each in turn for one condition of loading; then to add load and once more take all readings. It was found, however, much more satisfactory to keep the microscope in position for one member and to complete the two readings for it. This meant considerably more labour in loading and unloading than the other method, but was more accurate and reliable.

Having obtained a complete set of readings for the framework, certain checks were applied as follows:—

(i.) In the case of symmetrical loading the strain of the corresponding members on the two sides of the structure should be the same.

(ii.) The vertical components of the force in the members across any section should give the total vertical shear at that section. Thus in the centre of each bay the total of the vertical components of the loads in the cross bracing wires should give the shear across that bay.

(iii.) The forces in the members at each joint should give static balance.

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After the first set of readings had been taken it was found that the errors, as indicated by the out of balance forces at several joints, were of a serious character, and repeat readings were made with no better result. Further investigation indicated that the probable source of error was due to some of the strut members bending slightly, so that the resultant strain due to direct compression and bending stress was being measured and not the direct compression alone. Since the members were circular in section this trouble was overcome by taking readings of strain at the opposite ends of any diameter: the average then gave the strain due to direct compression stress alone. When this was done results were very much better and within the limits of experimental accuracy, and the method was therefore always adopted in measuring strains of tube members in later experiments.

Experimental Errors.

The main sources of possible error in obtaining experimental results are three in number, viz. :—

(i.) Errors due to the limitations of the method of measurement.
(ii.) Errors due to the variation in the sizes of the members of the structure.
(iii.) Errors in reading the instrument.

(i.) *Errors due to the limitations of the method.*

As already stated, one division of the micrometer head of the microscope corresponds to 1/17780 inch, and the magnification required entailed very delicate manipulation of the micrometer head if exact coincidence was to be obtained between the lines on the glass and on the member, and that on the traversing eyepiece. This, however, was principally a matter of practice, and after some experience it was found to be a comparatively simple matter to obtain satisfactory results, and observations could be repeated to within about one division of the micrometer head, which is therefore assumed to be the limit of experimental accuracy. This will be seen on reference to the calibration figures to correspond to ± 8 pounds on the standard tube members and ± 1 pound on the wires. The small error on the wires makes the results obtained for these members particularly reliable and useful. Another difficulty arose from vibration of the laboratory, and it was found impossible to take readings if

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plant were running in certain parts of the buildings, or if a heavy vehicle were passing outside. Such disturbances were, however, only occasional, and usually this trouble was not sufficiently serious to cause any prolonged interruption of the work.

(ii.) *Errors due to the variation in the size of the members.*

The structure was made of aircraft materials in which great care is taken to ensure uniformity of quality and dimensions. Tolerances, however, are unavoidable, and in the case of the tubes the variation in thickness allowed by specification amounts to 7 per cent., and due to this cause the error in the readings of any tubular member may be $\pm 3\frac{1}{2}$ per cent., while the corresponding error in the wires may be the same.

(iii.) *Errors in reading.*

Errors in reading the instrument were eliminated as far as possible by taking at least three measurements on each member. Even with this precaution, however, it was found that occasionally a wrong value for the strain was obtained, but this could always be detected by an application of the checks previously mentioned. Having obtained a complete set of readings for the structure, the out of balance force at each joint was expressed as components along three mutually perpendicular axes. If this out of balance force were serious, check readings were made in order to trace the error, but in the majority of cases the errors were within the limits of experimental accuracy. These errors were then distributed among the members of the structure at the joint concerned as far as was possible. This was of necessity a somewhat arbitrary matter, and the general method was to neglect the wires, since the area of these was only 1/10 of that of the tube members. The out of balance force was then distributed between the tube members. It was found that the corrections thus applied were always very small and never exceeded the amount by which the reading might have been in error due to the causes enumerated above.

Experimental Results.

In identifying the various members of the structure the following system has been adopted, and is shown on fig. 1. Each transverse frame is distinguished by a letter beginning at the fixed or wall end with A. Each joint in the transverse is numbered, beginning at the bottom with 1 and

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following round the frame in a clockwise direction viewed from the free end. The middle joint in a transverse frame is 0. Thus each joint in the structure is denoted by a letter and a numeral suffix, *e. g.* A_4, B_3, etc. A positive sign is used to denote a tensile load and a negative to denote a compressive load.

Part I.

Experiments on the framework subjected to a constant shear and uniformly varying bending moment for comparison with the theoretical results obtained by an application of the Principle of Least Work.

Experiment 1.

All longitudinal members 7/8 in. O.D. × ·028 in.
End bulkhead radially braced with 4 B.A. rods.
No bulkhead bracing in remaining transverse frames.
Single load of 400 lb. applied at end bulkhead joint D_4.

The two sides of the structure gave practically exact agreement, differences being only of the order of experimental errors. The shears were also satisfactory, and under these circumstances the strains in the wires only were measured for comparison with the theoretical values. The results are given in Table I., which also gives the theoretical values.

Table I.

Member.	Load as measured. lb.	Calculated load. lb.	Difference. lb.
A_4B_5	− 75·5	− 70·8	+ 4·7
A_5B_4	35·5	27·2	+ 8·3
A_5B_6	−103·7	−106·0	− 2·3
A_6B_5	103·5	106·0	− 2·5
A_6B_1	− 26·75	− 27·2	− 0·5
A_1B_6	69·9	70·8	− 0·9
B_4C_5	− 70·5	− 62·0	+ 8·5
B_5C_4	38·5	36·0	+ 2·5
B_5C_6	−103·5	−106·0	− 2·5
B_6C_5	103·0	106·0	− 3·0
B_6C_1	− 40·6	− 36·0	+ 4·6
B_1C_6	61·8	62·0	− 0·2
C_4D_5	− 59·6	− 53·3	+ 6·3
C_5D_4	57·4	44·6	+12·8
C_5D_6	−102·8	−106·0	− 3·2
C_6D_5	102·3	106·0	− 3·7
C_6D_1	− 44·6	− 44·6	0
C_1D_6	50·0	53·3	− 3·3

It will be seen that there are appreciable differences

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between the measured and theoretical loads in the members, the characteristic being that the loads in the wires of the top panels, that is C_4D_5, C_5D_4, etc., are larger than calculated, while the loads of the remaining wires are smaller.

This is the result which would be expected if the end bulkhead were distorting in its own plane, and it was therefore decided to substitute much heavier bracing in the end bulkhead in place of the 4 B.A. wires used in this experiment, in order to approximate more nearly to the conditions of rigidity assumed in the mathematical investigation.

Experiment 2.

All longitudinal members 7/8 in. O.D. × ·028 in.

End bulkhead radially braced with 5/8 in. diameter solid steel rods.

No bulkhead bracing in other transverse frames.

Single load of 400 lb. applied at end bulkhead joint D_4.

The radial members in the end bulkhead, which had previously been 4 B.A. swaged rods, were replaced by 5/8 inch diameter steel rods, each rod being provided with a turnbuckle for tightening up. It was considered that this gave as close approximation to a rigid bulkhead as could be conveniently obtained, and should afford clear evidence as to whether the discrepancy between the measured and theoretical loads found in the previous experiment were due to the elastic deformation of the bulkhead in its own plane, or to other causes. Agreement between the two sides of the structure was excellent as well as the results obtained for shear, and a comparison of the measured and theoretical values of the loads in all cross bracing members is given in Table II. One side only of the structure is given, the loads being the average of the two sides in each case.

It will be seen that good agreement between the measured and the calculated loads was obtained throughout the structure. In only one case does the difference exceed 2 pounds.

Comparing these results with those of Table I., it is clear that the elasticity of the end bulkhead is an appreciable factor in the distribution of loads in the members of the structure.

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TABLE II.

Member.	Measured load. lb.	Calculated load. lb.	Difference. lb.
A_4B_5	− 72·8	− 70·8	+2·0
A_4B_4	27·5	27·2	+0·3
A_5B_6	−106·5	−106·0	+0·5
A_5B_5	104·5	106·0	−1·5
A_6B_1	− 27·1	− 27·2	−0·1
A_5B_6	68·4	70·8	−2·4
B_4C_5	− 63·5	− 62·0	+1·5
B_4C_4	36·7	36·0	+0·7
B_5C_6	−105·0	−106·0	−1·0
B_5C_5	107·6	106·0	+1·6
B_6C_1	− 35·7	− 36·0	−0·3
B_6C_6	63·2	62·0	+1·2
C_4D_5	− 52·0	− 53·3	−1·3
C_4D_4	45·8	44·6	+0·8
C_5D_6	−105·5	−106·0	−0·5
C_5D_5	105·0	106·0	−1·0
C_6D_1	− 43·8	− 44·6	−0·8
C_6D_6	53·1	53·3	−0·2

Experiment 3.

Keel members $A_4B_4C_4D_4$ 7/8 in. diameter solid steel bars.
Other longitudinal members 7/8 in. O.D. × ·028 in.
End bulkhead radially braced with 4 B.A. swaged rods.
Remaining bulkheads unbraced.
Single load of 400 lb. applied at joint D_4.

In this experiment the keel member, which had hitherto been the same size as the other longitudinal members, was made of solid steel bar 7/8 inch diameter, attached to the joints by dowels in the same manner as the other tubular members. In this case the loads in all the members were measured, and not only those in the wires. Good agreement was obtained between the two sides of the structure. The shears were practically exact, and the corrections necessary to give static balance at the joints were in all cases less than the equivalent of one division of the micrometer head (Table III.).

This case was analysed theoretically, and it will be seen that the agreement between calculation and experiment is very good. In view of the closeness of this agreement, it was considered unnecessary to repeat the experiment with a stiffer end bulkhead. It will be clear from a consideration of the earlier results that such alteration would tend still further to reduce the errors between measured and calculated loads. Owing to the size of the keel member, which was

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approximately ten times the area of any other longitudinal, the strains in that member were too small to be measured satisfactorily, and the figures given in brackets have been deduced from consideration of static balance at the joints.

TABLE III.

Member.	Measured load. lb.	Correction for balance. lb.	Corrected reading. lb.	Calculated load. lb.	Difference. lb.
A_1B_1	330·0	3·2	333·2	337·8	−4·6
A_2B_2	180·5	−1·0	179·5	177·3	+2·2
A_3B_3	−119·6	3·9	−115·7	−116·4	−0·7
A_4B_4	—	—	(−510·0)	−506·8	+3·2
A_1B_2	67·9	—	67·9	67·6	+0·3
A_2B_1	− 27·5	—	− 27·5	− 28·0	−0·5
A_2B_3	102·5	—	102·5	100·8	+1·7
A_3B_2	− 96·4	—	− 96·4	− 96·2	+0·2
A_3B_4	60·1	—	60·1	60·4	−0·3
A_4B_3	− 74·4	—	− 74·4	− 74·0	+0·4
B_1B_2	− 17·6	−4·0	− 21·6	− 20·0	+1·6
B_2B_3	− 3·9	1·2	− 2·7	− 2·5	+0·2
B_3B_4	7·8	0·8	8·6	7·0	+1·6
B_1C_1	204·0	−6·4	197·6	202·4	−4·8
B_2C_2	109·1	0·9	110·0	106·4	+3·6
B_3C_3	− 66·8	−0·9	− 67·7	− 69·6	+1·9
B_4C_4	—	—	(−306·0)	−304·0	+2·0
B_1C_2	60·7	—	60·7	59·6	+1·1
B_2C_1	− 36·7	—	− 36·7	− 36·0	+0·7
B_2C_3	98·5	—	98·5	99·8	−1·3
B_3C_2	− 97·4	—	− 97·4	− 96·8	+0·6
B_3C_4	63·1	—	63·1	63·0	+0·1
B_4C_3	− 72·7	—	− 72·7	− 71·2	+1·5
C_1C_2	− 7·8	−2·0	− 9·8	− 10·0	−0·2
C_2C_3	− 3·9	4·0	0·1	− 1·2	+1·3
C_3C_4	3·9	−0·5	3·4	3·5	−0·1
C_1D_1	70·6	−5·5	65·1	67·2	−2·1
C_2D_2	35·3	2·7	38·0	35·2	+2·8
C_3D_3	− 19·6	−4·1	− 23·7	− 23·2	+0·5
C_4D_4	—	—	(−104·0)	−101·2	+2·8
C_1D_2	49·5	—	49·5	51·8	−2·3
C_2D_1	− 42·3	—	− 42·3	− 43·8	−1·5
C_2D_3	99·2	—	99·2	98·8	+0·4
C_3D_2	− 98·9	—	− 98·9	− 98·0	+0·9
C_3D_4	67·6	—	67·6	66·0	+1·6
C_4D_3	− 68·4	—	− 68·4	− 68·6	−0·2
D_1D_2	− 35·3	−2·0	37·3	− 37·0	+0·3
D_2D_3	58·9	−0·5	58·4	59·0	−0·6
D_3D_4	161·0	4·0	165·0	166·0	−1·0
D_0D_1	65·3	—	65·3	—	—
D_0D_2	3·5	—	3·5	—	—
D_0D_3	−122·0	—	−122·0	—	—
D_0D_4	191·8	—	191·8	—	—

The members D_0D_1, D_0D_2, D_0D_3, and D_0D_4 are the radial wires in the end bulkhead, and since these are considered to

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be rigid in the theoretical analysis no separate values can be calculated. The analysis does, however, permit certain differences to be obtained, and these are given in Table III. *a*, together with the measured differences.

TABLE III *a*.

Difference.	Measured value. lb.	Calculated value. lb.	Difference. lb.
$D_0D_2-D_0D_4$	−188·3	−187·6	+0·7
$D_0D_1-D_0D_4$	−126·2	−126·5	−0·3

PART II.

Experiments on the framework subjected to a pure torque.

The theoretical analysis for the stresses in a redundantly braced tube when subjected to a pure torque * indicates that the panel bracing members alone are brought into operation, and no stresses are put into the longitudinal members or transverse struts.

In the theoretical investigation it is assumed that the external loading is applied in the particular manner which prevents any distortion of the transverse frame, and also that the structure is pin-jointed throughout. Transverse frames which were plane before loading are then shown to remain plane in the strained condition of the structure.

The following experiments were carried out to determine the degree of accuracy obtained in an actual structure compared with calculations based on the above analysis, and also to discover the effect of varying the elasticity of the bulkhead bracing in the transverse to which the torque was applied when the external loading, although giving a resultant pure torque, was not applied to the joints as hypothecated in the analysis.

The structure used was the hexagonal frame already described, fitted with a solid 7/8 inch diameter steel keel member and no pyramidal nose-piece.

The torque was applied by loads at the joints D_3 and D_6, into which special swivel hooks were screwed. An upward load was applied at D_3 by means of the weighing balance used in the shearing-force experiments, and weights were

* Aeronautical Research Committee, R & M 791.—Southwell.

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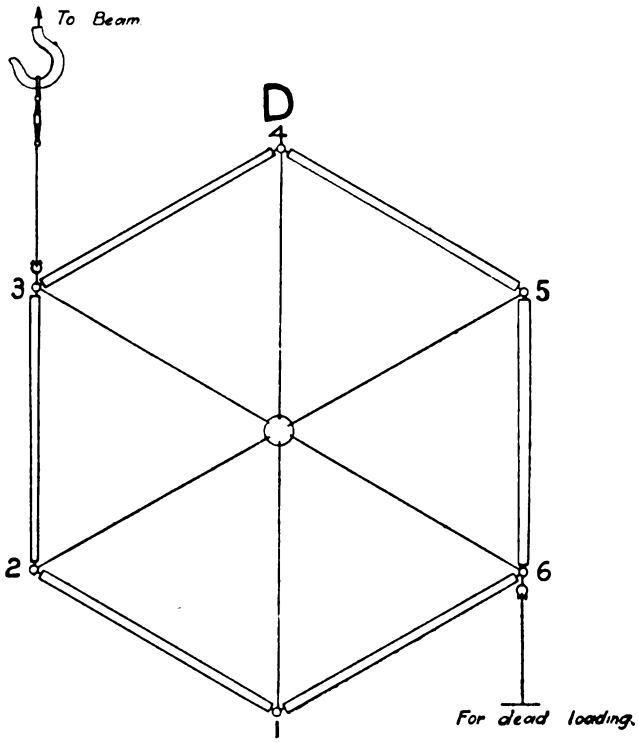
hung from D_6 (fig. 4). An initial load was applied to D_6 equal to the weight of the scale-pan which was transmitted to D_3.

Fig. 4.



The methods adopted in the experiments were exactly as described in the earlier work.

The increment of load in each case was 280 lb. upward at D_3, and 280 lb. downwards at D_6, giving a torque of 12124 inch-lb.

Experiment 4.

End bulkhead radially braced with 5/8 in. d ameter solid steel rods.

Other bulkheads unbraced.

This experiment reproduces as nearly as possible the theoretical conditions, since the approximately rigid bulkhead bracing serves to distribute the torque in a manner corresponding to that required by the analysis.

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The theoretical load in each of the panel wires is 72·8 lb., and the closeness of the experimental results to this will be seen from Table IV., which gives the measured loads in all these members.

There are small departures from the theoretical figures, but these balance each other as will be seen from the average load in the wires of each bay.

In bay AB. Average load = 72·54 lb.
In bay BC. Average load = 73·58 lb.
In bay CD. Average load = 72·38 lb.

TABLE IV.

Member.	Measured load. lb.	Member.	Measured load. lb.
A_1B_2	74·5	A_4B_5	71·5
A_2B_1	−71·5	A_5B_4	−72·5
A_2B_3	74·5	A_5B_6	72·5
A_3B_2	−70·5	A_6B_5	−71·5
A_3B_4	72·5	A_6B_1	73·5
A_4B_3	−72·0	A_1B_6	−73·5
B_1C_2	74·5	B_4C_5	71·5
B_2C_1	−73·5	B_5C_4	−72·5
B_2C_3	72·5	B_5C_6	73·5
B_3C_2	−74·5	B_6C_5	−74·5
B_3C_4	75·5	B_6C_1	73·5
B_4C_3	−73·5	B_1C_6	−73·5
C_1D_2	73·5	C_4D_5	74·5
C_2D_1	−70·5	C_5D_4	−71·0
C_2D_3	70·5	C_5D_6	71·5
C_3D_2	−73·5	C_6D_5	−71·5
C_3D_4	71·0	C_6D_1	74·0
C_4D_3	−73·5	C_1D_6	−73·5

Experiment 5.

End bulkhead radially braced with 4 B.A. swaged rods.
Other bulkheads unbraced.

In this experiment the elasticity of the transverse bracing was modified, but, as will be seen from the results in Table V., the measured loads were of the same degree of accuracy as with the nearly rigid bracing of the two previous experiments.

In bay AB. Average load = 72·92 lb.
In bay BC. Average load = 72·83 lb.
In bay CD. Average load = 73·04 lb.

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TABLE V.

Member.	Measured load. lb.	Member.	Measured load. lb.
A_1B_2	71·5	A_4B_5	73·5
A_2B_1	−73·5	A_5B_4	−72·0
A_2B_3	72·0	A_5B_6	73·0
A_3B_2	−74·5	A_6B_5	−73·5
A_3B_4	71·0	A_6B_1	73·5
A_4B_3	−75·5	A_1B_6	−71·5
B_1C_2	74·5	B_4C_5	74·5
B_2C_1	−71·0	B_5C_4	−73·5
B_2C_3	74 5	B_5C_6	71·5
B_3C_2	−73·5	B_6C_5	−74·5
B_3C_4	71·5	B_6C_1	71·5
B_4C_3	−73·0	B_1C_6	−70·5
C_1D_2	74·5	C_4D_5	73·0
C_2D_1	−70·5	C_5D_4	−72·5
C_2D_3	75·5	C_5D_6	74·5
C_3D_2	−71·5	C_6D_5	−73·5
C_3D_4	71·5	C_6D_1	73·5
C_4D_3	−74·5	C_1D_6	−71·5
D_0D_4	10·2	D_0D_5	−81·6
D_0D_6	104·5		

X. *The Motion of an Air Bubble rising in Water.* By OTOGORÔ MIYAGI, *Professor of Hydraulics and Hydraulic Engineering in the Tôhoku Imperial University, Sendai, Japan* *.

[Plate III.]

ABSTRACT.

Air bubbles of various sizes moving up in still water are carefully treated experimentally and then theoretically. Their terminal velocities are determined in relation to their sizes, and the changes of their shapes during their motion are investigated.

The mass of water carried up with a moving bubble and the resistance to its motion are determined, and the most probable equation of motion is proposed. It is also proved that there are two different kinds of motion of a bubble in water exactly analogous to the stream-line and the turbulent flows of a viscous fluid, which passes from the one to the other distinctly at the critical radius of the bubble.

* Communicated by the Author.

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1. Introductory.

AIR bubbles are formed in water naturally or artificially. As in a water-turbine or a pump, atmospheric air naturally mixed with water expands to form large bubbles in the space where the pressure is very low, as in the draught- or suction-tube, which destroy the effective action of the machine. As in an air-lift pump, air is purposely admitted in the water deep in a well to make it form bubbles rising in the eduction pipe, and their sizes and forms affect greatly the action of the pump.

The forces acting on an air bubble rising in water may be classed as the surface tension, the upward force due to buoyancy, and the resistance to motion offered by the surrounding water.

The surface tension acts to keep the bubble spherical as the most stable form, while the resistance makes it deform in a flattened shape, and, owing to the result that it moves up with the minimum resistance acted upon, it shows some peculiar outline as to its form and passage.

The smaller the bubble, the larger the effect of surface tension to keep it spherical becomes in comparison with the resistance, the more it resembles a true spherical shape and the more stable it is. When the bubble is large, the effect of the surface tension is small compared with the resistance, and it displays some peculiarly flattened outline, which is very unstable, changing its shape momentarily with some oscillating features.

A very small bubble, therefore, may be regarded approximately as a sphere, and, with some suitable assumptions, its motion may be treated mathematically; but for a large bubble as is common in practical cases the simple mathematical treatments cannot by any means be applied in order to solve even approximately its motion in water.

The present object is, for an air bubble of a practical size, to study its motion in water from accurate experiments and to find the law of resistance connected with mathematical considerations. For very small bubbles up to the radius of 0·0385 cm. valuable experiments have already been carried on by Mr. H. S. Allen *, which will be referred to later on.

* Phil. Mag., Sept. and Nov. 1900.

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II. Description of the Experimental Apparatus.

The apparatus consisted of an experiment vessel, a recording drum, a flash-light apparatus, and a tuning-fork.

The experiment vessel was made of two rectangular flat glass plates about 13 cm. in width and 30 cm. in height, set vertically and secured firmly by a metal holder about 2·4 cm. apart to form a transparent rectangular box to retain water, in which an air bubble was made to rise.

The recording drum was a cylindrical drum of 20 cm. in diameter and 26 cm. in height, made of aluminium casting, which was caused to rotate by an electric motor. This drum was set vertically and rotated horizontally with a bromide paper to be used in an ordinary photographic process wrapped round it. A stationary cylindrical case of about 22 cm. in diameter made of copper plate was set concentric to enclose the drum to protect the bromide paper against any light. A vertical window extending about the whole length of this case in the form of a narrow slit was made in it, the width of which was made adjustable by a sliding door in contact with the window, through which the bromide paper was exposed to the flash-light.

The flash-light apparatus consisted of a 500 candle-power incandescent lamp encased in a wooden box and a rotating disk. The disk was made of a wooden plate of 45 cm. in radius, and it had eight radial slots each of 2 cm. in width and 25 cm. in radial length uniformly spaced. This was placed about 60 cm. in front of the box to rotate in a vertical plane with a horizontal shaft by an electric motor. On the front face of the box there was made a vertical slot of 3 cm. in width and 25 cm. in length, through which the light from the incandescent lamp was projected on the face of the disk, which was so placed that at the moment that the slot on the disk came in line with that on the box a flash of light was passed through the disk to project it on the bromide paper through the vertical window mentioned above.

The tuning-fork was used to record accurately the velocity of rotation of the recording drum. It was one of a frequency of 82 vibrations per sec. A small mirror was put on its edge by which the light from a point-light was reflected on the bromide paper. The point-light was encased in a box furnished with a small hole fitted with a convex lens to lead the light through it, and a second convex lens was placed in front of the hole by means of which the point-light image was focussed on the bromide paper to get a fine wave-line on

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it, by which the time of rotation of the recording drum was accurately recorded.

Figs. 1 and 2 show diagrammatically the elevation and the plan respectively of the experimental apparatus. The adjustable window in the stationary protecting case set concentric with the recording drum was set in line with the incandescent lamp, and the experiment vessel was placed immediately in front of it. The tuning-fork was so

Fig. 1.

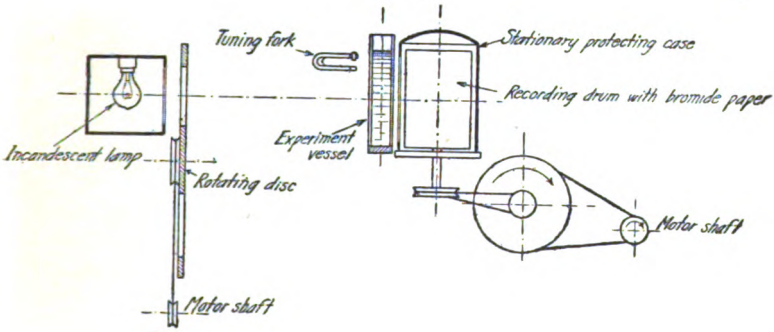
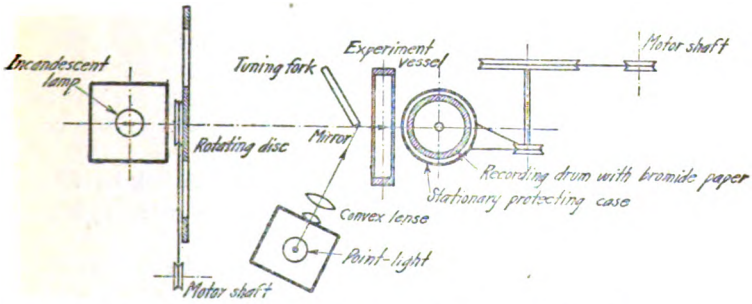


Fig. 2.



placed in front of this vessel that the point-light image was projected on the bromide paper through the water space.

The experiment vessel was placed as near as possible to the recording drum, while the flash-light apparatus was set far away from it in order to get an approximately horizontally projected shadow of the air bubble on the bromide paper. Actually the distance from the bromide paper to the centre line of the experiment vessel was about 2·3 cm., and that to the incandescent lamp was about 156 cm., so that the error deviating from the horizontal projection was almost negligible.

All the above apparatus were set up in a dark room.

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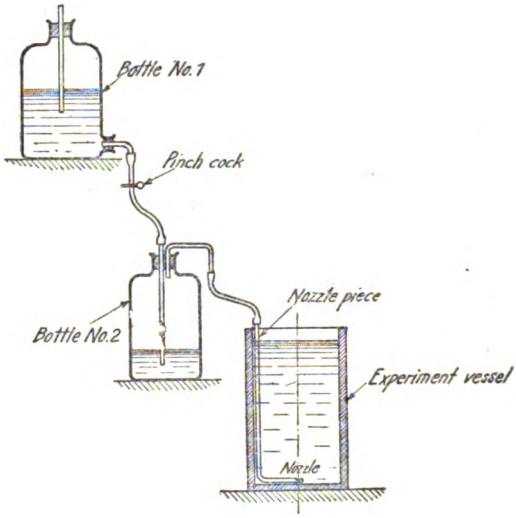
III. Method of making a Bubble.

Fig. 3 is a diagrammatic view showing the method of making a bubble in the experiment vessel. The bottles No. 1 and No. 2 were set at different levels, and they were connected

Fig. 3.



by an india-rubber tubing fitted with a pinch-cock by which the formation of the bubble at the nozzle was regulated at will.

The nozzle-piece was made of a fine glass tube bent at right angles, closed at the end, and it was connected to bottle No. 2 by an india-rubber tubing as shown in fig. 3. Near the closed end of this nozzle-piece a nozzle was made, which was formed by grinding off cylindrically by a bar with emery-powder so as to open a sharp-edged mouth, the elevation and the plan of which are shown in fig. 4. The sizes of bubbles being dependent on the sizes of the nozzle, several nozzle-pieces of different diameters with different sizes of nozzles were made.

The nozzle-piece was sunk into the water in the experiment vessel, as shown in fig. 3, setting the nozzle at the centre of the vessel near its bottom. Special care was paid in this case in order to set the edge of the nozzle symmetrically

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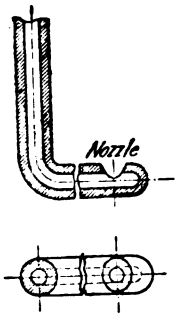
about the vertical axis, which was absolutely necessary to get a symmetrical bubble free from initial disturbance.

Fig. 4.



Such a bubble would rise initially vertically upwards, otherwise it would rise in an inclined direction with an initial impulsive disturbance which had a great influence on its motion.

IV. Measurement of the Sizes of Bubbles.

On opening the pinch-cock slightly the water in the nozzle-piece would be first expelled slowly from the nozzle by the pressure of the air and then the air would appear at the nozzle which gradually grew large and finally separated from it as a free bubble.

On watching the formation of the bubble carefully, adjusting the pinch-cock so that the bubble was formed as slowly and steadily as possible, it was observed that its convex top gradually swelled from a hemisphere to a sphere just at the moment of leaving the nozzle. A microscope with a measuring scale inside was set horizontal to observe this action and to measure the diameters of such spherical bubbles just at the moment of their leaving the nozzle.

Bubbles successively formed from a given nozzle leaving the pinchcock untouched being observed to be the same in all respects, the experiment was made on a bubble which was formed a little after the one the diameter of which was measured.

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V. Method of Conducting Experiment.

The speeds of the electric motors to drive the recording drum and the rotating disk were adjusted previously to suit the experiment. These speeds had to be in a good relation with the amount of the opening of the adjustable window made on the stationary protecting case to get fine successive photographs of a bubble on the bromide paper.

The water in the experiment vessel was saturated with air previous to the experiment causing air bubbles to rise in it for a long time, in order to avoid the absorption of air from the bubble in the course of the experiment.

Now, for conducting an experiment, a bromide paper was secured firmly around the recording drum with cramps arranged to it, and the protecting case was put on it with adjustable window closed. The pinch-cock was adjusted to give off successive bubbles very slowly in the water in the experiment vessel, and the diameter of one of them was measured accurately by the measuring microscope, the process being made under a red or ordinary incandescent lamp as the case might be. The temperature of the water was read on the thermometer inserted in the experiment vessel.

The adjustable window was then opened to the amount previously adjusted, the electric motors were started and the tuning-fork was set in action. The 500 candle-power incandescent and the point-light lamps were now lighted at as nearly the same time as possible, and they were put out after the recording drum had made about a complete rotation.

The protecting case was then removed, the bromide paper was taken off, and the only thing remaining was to develop this bromide paper. This was done in the same room after each experiment was performed.

VI. Experimental Results.

Terminal Velocity with which a Bubble rises vertically upwards.—Figs. 1 to 5 (Pl. III.) show some of the photographic pictures taken by developing the bromide paper as above mentioned with a reduced scale. (The complete sheet of a bromide paper contains usually one or more than one of such pictures arranged in series by successive bubbles which rise almost periodically one after the other. Here we have shown one of them taken out of each sheet.) Each of them shows the successive shapes and positions of a bubble distributing between the successive photographs of the nozzle used and one continuous vibration curve of the tuning-fork.

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The shadows of the nozzle and the bubble obviously being projected at the same time by one flash, the successive photographs of the nozzle and the correspondiug photographs of the bubble will be easily pointed out on a given picture. The number of vibrations of the tuning-fork between any two consecutive photographs of the nozzle being directly counted on it, the time occupied by the bubble to move from one position to the next can be easily determined, and the vertical distance between any two consecutive photographs of the bubble divided by this time will be the mean vertica velocity at that position.

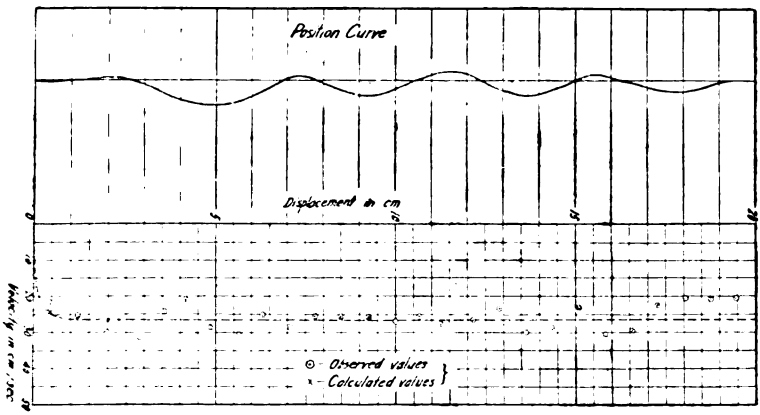

Fig. 5.

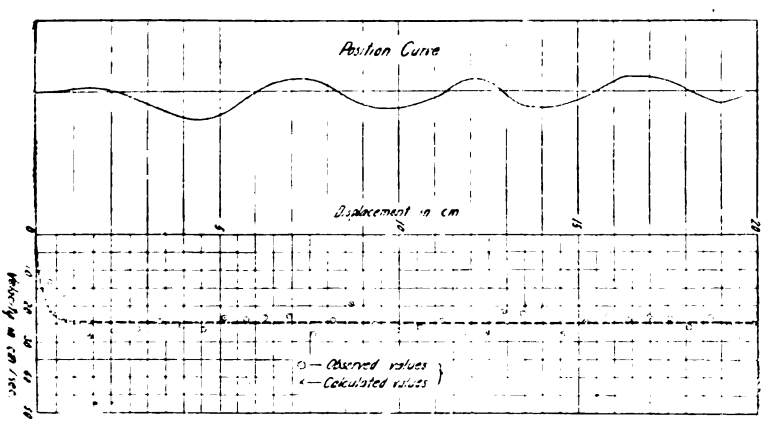

Fig. 6.

Such velocities were calculated at every position of the bubble on each picture, and they are plotted on a squared paper against the displacement or the height of the bubble above the nozzle to show diagrammatically the velocities of

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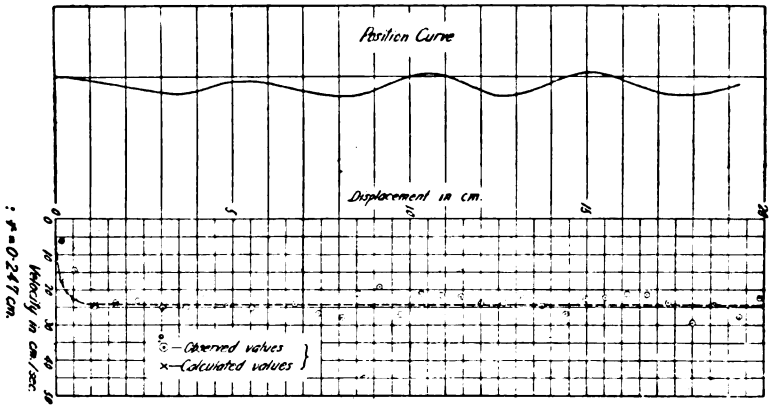

Fig. 7.

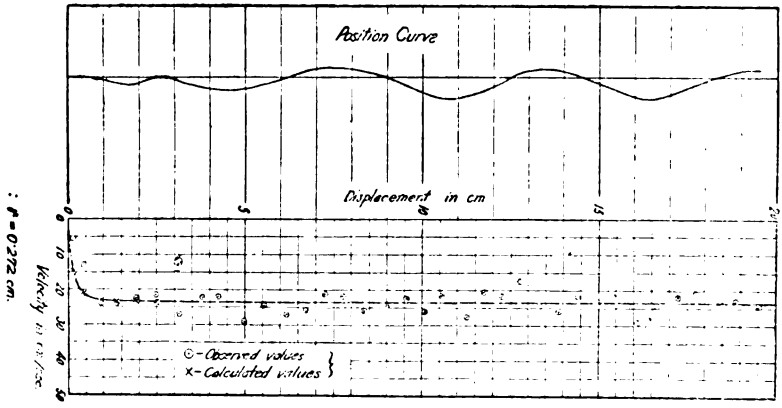

Fig. 8.

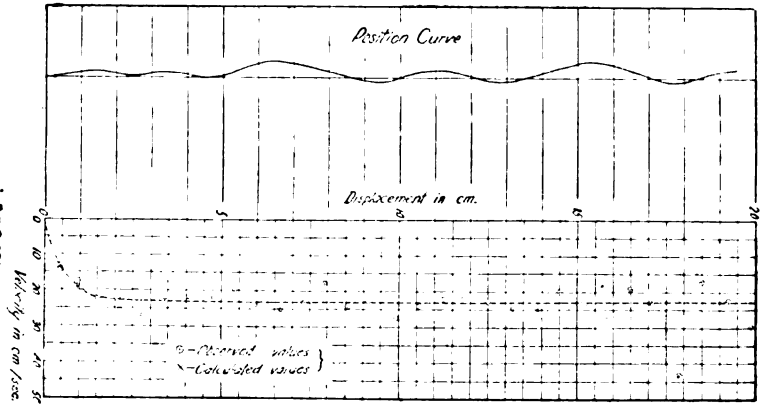

Fig. 9.

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the bubble with respect to its positions. Figs. 5 to 9 show some of such diagrams, the averaging curve being drawn on each of them, and we can see from these curves that all the bubbles attain their constant terminal velocities almost as soon as they have left the nozzle.

As the effect of the depth of water on the size of the bubble in the present experiment was negligibly small and was assumed to be unchanged during its passage, the above fact shows that for a bubble of a given size there is always a fixed velocity of rise. Table I. gives the experimental results showing the relation between the sizes of bubbles and their terminal velocities.

Fig. 10.

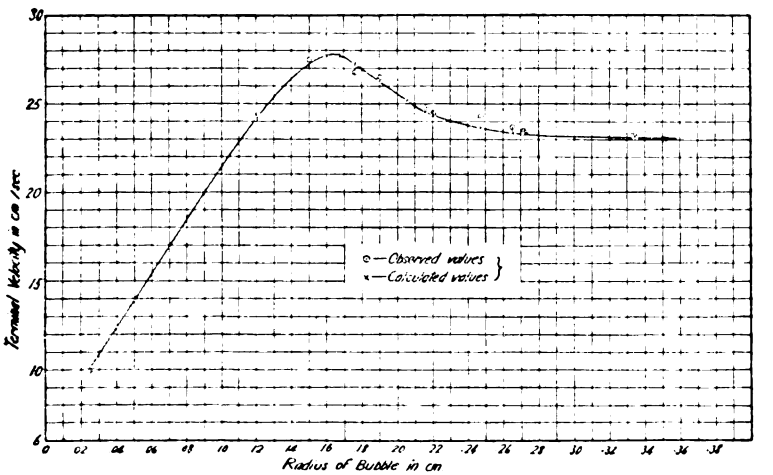

Fig. 10 shows the above results by a curve, on which the points with circular marks are those plotted in accordance with the experiments, and those with cross marks are those calculated from the formula deduced by the writer to be explained later on.

For very small bubbles, as up to the radius of 0·0385 cm. Mr. Allen gave a straight-line relation between their radii and velocities, and according to the present experiment, with reference to fig. 10, his conclusion may be acknowledged to extend approximately to one of the radius of about 0·12 cm. without appreciable error, although we have no experimental results of bubbles of the sizes lying between the radii of

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0·025 cm. and 0·12 cm. to prove the statement owing to the difficulty of making such small bubbles.

For larger bubbles than the radius of about 0·12 cm. the velocities increase in a less ratio than proportional with their radii showing some curvature in the curve, and soon after there occurs a maximum velocity of about 27·8 cm. per sec. corresponding to a bubble of the radius of about 0·165 cm. Then the curve falls and tends to be directed horizontally, showing that the velocity decreases contrary to the radius and tends to a final constant velocity of about 23·1 cm. per sec. for bubbles larger than a radius of about 0·33 cm.

The above results are of course dependent on the temperature of the water which has an influence on the viscous resistance to the motion of bubbles, but under the range of temperature experienced by the present experiments, the temperature effect on the viscosity of the water being negligibly small, they can be taken as correct for water at an average of 18° C.

We may infer from the above phenomena that when the bubble is very small the buoyancy increases in the same proportion as the resistance showing the velocity increasing proportionally with its size, and there is a limit of proportionality, after which the resistance comes to act with an increasing proportion to its buoyancy, and at the end of which the velocity shows its maximum value. Then the velocity decreases contrary to its size owing to the rapidly increasing resistance, which tends gradually to the state of counterbalancing of the resistance with the buoyancy, showing a final constant velocity irrespective of its size.

When the bubble is very small it is considered to assume nearly a stable spherical shape, as already mentioned, and its velocity curve is shown by the straight ascending part in fig. 10. When the bubble is sufficiently large its shape deviates greatly from the sphere which is exposed to the greater proportional resistance, and its velocity curve is shown by the descending part in fig. 10. When the bubble is very large it becomes very unstable, subjected to the greater resistance and buoyancy, and its velocity is shown by the straight horizontal part in fig. 10. Such a large bubble has a tendency to divide into smaller ones.

Course of a Bubble.—If a bubble should rise on a vertical straight course, the centre of its photograph in figs. 1 to 5 (Pl. III.) would have to be in the vertical line drawn at the centre of the corresponding photograph of the nozzle in all its positions. In order to test this, vertical lines were drawn at

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the centres of the successive photographs of the nozzle on each photographic picture as shown in figs. 1 to 5 (Pl. III.) and it was found that the photographs of a bubble did not lie on such lines, some being on the right and others being on the left, indicating that the course of the bubble was never a vertical line. It loiters about that line, dashing in every direction, tracing a course like a helix round it, as observed from the top of the experiment vessel looking down into the water.

To see such a course, the successive positions of the centre of a bubble were plotted about a vertical line, and we obtained the diagram as shown on the left-hand space in figs. 5 to 9, by which it can be easily understood how it loiters about the line as it ascends through the water. This, of course, shows its projection on a vertical plane parallel to the face of the experiment vessel, and supposing such a course to be shown also on a vertical plane perpendicular to the above, the course traced in space can be imagined to be a kind of helix.

Variation of the Shape of a Bubble in its Course.—If a bubble always kept a regular symmetrical shape in all respects about the vertical line through its centre of gravity, its course would be a vertical line. The shape, however, is never symmetrical owing to the very slight initial disturbance which by no means can be avoided as a practical problem, and it traces a course as explained above about the vertical line.

The deviation of its course from a vertical line thus being due to its deformation from symmetry, there must be a certain relation between the change in its shape and the position in its course. For the purpose of testing this, with some comparatively large bubbles in order to see it clearly, the outline shapes of each of the bubbles were carefully traced and put on the corresponding positions plotted about a vertical line as shown in fig. 11, by which we can see, at a glance, that there are certain regular changes of shape along their courses, and after a close observation we can find that the major axis of any bubble is always perpendicular to its course, that is, it moves always with its flattened face directed ahead, the reason of which can be explained as follows :—

Fig. 12 is a diagrammatical sketch showing the successive changes of the shape of a bubble along its upward course, assuming the motion to occur in a two-dimensional space. Suppose a bubble at the position A to dash or to move in the

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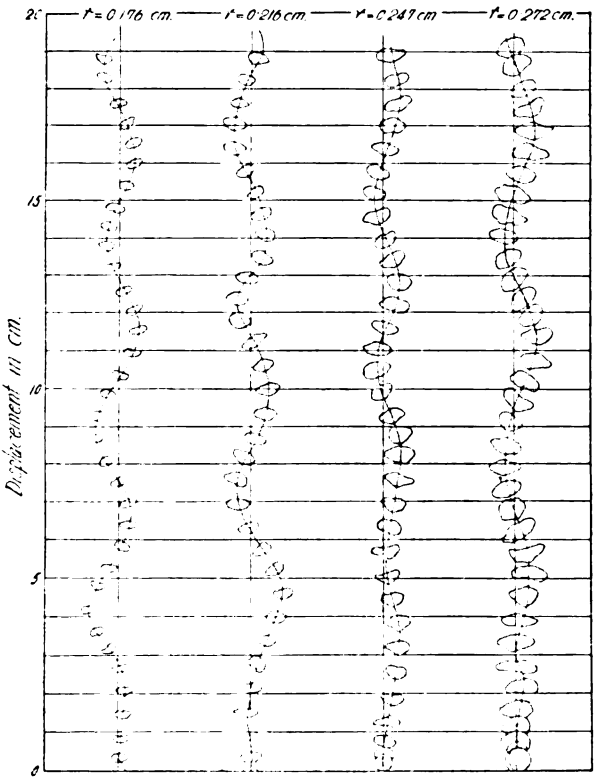
inclined direction AB to the vertical XY, acted upon by some practically unavoidable initial disturbance, then the resistance acting upon the front face of the bubble retards its motion, and makes it flat in the direction AB and pause for a while at the position B. The course will now change in the

Fig. 11.



direction BC by the action of gliding, due to its buoyancy, at first accelerating and then retarding, changing its shape from B to C with the flattened face directed towards BC, and it pauses again at the position C. Then its course will change in the direction CD and then in the direction DE, alternately repeating a similar movement, showing a resultant zig-zag passage like ABCDEF about the vertical XY.

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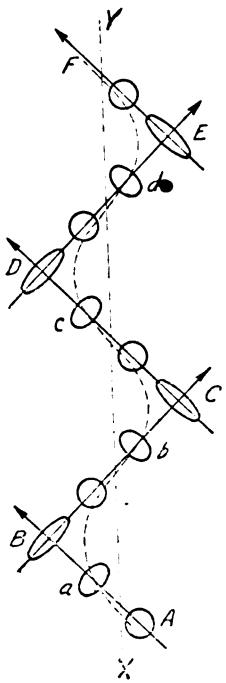
The above is the result of the two-dimensional motion. In a three-dimensional space, however, the bubble does not go so far as such positions as B, C, D, E where it pauses for a while, but it continues its motion round the vertical XY,

Fig. 12.



keeping its shape flattened in the direction of motion by the head resistance as shown at *a*, *b*, *c*, *d*, etc. The course of the bubble, therefore, is a helix round the vertical as shown with a broken line, and it keeps its major axis always perpendicular to this course.

VII. Theoretical Investigation.

Comparison of Stokes' and Allen's Conclusions.—From the measurement of terminal velocities of small bubbles Mr. Allen * has given his conclusions that the terminal velocity acquired by a small bubble ascending through a viscous fluid is the same as that which would be acquired by a solid

* Phil. Mag., Sept. and Nov. 1900.

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sphere, and that when the motion is very slow the velocity of a bubble agrees with that deduced from theoretical considerations by Stokes, and for greater velocities he has given his own formula. His experiments, however, were limited to very small bubbles up to a radius of 0·0385 cm. As for the motion of a solid sphere in a viscous fluid there are many authorities, such as G. Stokes, R. S. Woodward, H. S. Allen here mentioned and others, but there are few who have treated air bubbles of practical sizes, a subject most useful from the practical point of view.

The formula introduced by Stokes is as follows :—

$$v=\frac{2}{9}gr^2\frac{\rho-\sigma}{\eta}\frac{\beta r+3\eta}{\beta r+2\eta},$$

where v=constant velocity (terminal velocity),
r=radius of the sphere,
η=viscosity of the liquid,
β=coefficient of the sliding friction,
ρ=density of the liquid,
and σ=density of the sphere.

Under the assumption that there is no slipping on the surface of the sphere assuming a capillary flow, β is infinity, and writing $\eta=\mu\rho$, so that μ is the kinematic coefficient of viscosity, we shall have

$$v=\frac{2}{9}gr^2\frac{\rho-\sigma}{\mu\rho}\,*, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

which shows that the terminal velocity varies as the square of the radius of the sphere, the velocity curve against the radius being a parabola.

For greater velocities exceeding a definite critical value, Allen has deduced the formula :

$$v=\frac{1}{2}\left(\frac{\rho-\sigma}{\rho}g\right)^{\frac{2}{3}}\frac{r-\frac{2}{5}\bar{r}}{\mu^{\frac{1}{3}}},$$

where $\bar{r}$ is the value of r which makes $vr=\mu$, so that when β is infinity it gives such a value as is expressed by

$$\bar{r}^3=\frac{9\mu^2\rho}{2g(\rho-\sigma)}.$$

Allen's formula will be, therefore,

$$v=\frac{1}{2}\left(\frac{\rho-\sigma}{\rho}g\right)^{\frac{2}{3}}\left\{\frac{r}{\mu^{\frac{1}{3}}}-\frac{2}{5}\left[\frac{9\mu\rho}{2g(\rho-\sigma)}\right]^{\frac{1}{3}}\right\}, \quad . \quad . \quad (2)$$

and this shows that the terminal velocity varies linearly as the radius of the bubble.

* Whetham, Phil. Trans. 1890, and Allen, Phil. Mag., Sept. and Nov. 1900.

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Table II. gives the velocites of air bubbles moving upwards in water calculated from the above formulæ and the corresponding actual ones measured from the experiments. From this table we can at once observe that Stokes' parabolic

TABLE I.

Temperature, Deg. C.	14	18	26	18·8	23·7	12	14	12	15	21	18	23	21
Radius of Bubble, cm.	·025	·12	·15	·176	·19	·205	·216	·22	·247	·265	·272	·334	·351
Velocity of Bubble, cm./sec.	9·85	24·5	27·5	26·75	26·5	25·5	24·85	24·5	24·3	23·75	23·5	23·35	23·0

TABLE II.

Temperature, Deg. C.	14	18	26	18·8	12
Radius of Bubble, cm.	·025	·12	·15	·176	·205
Velocity in cm./sec. (observed)	9·85	24·5	27·5	26·75	25·5
Velocity in cm./sec. (calculated from Stokes' formula)	11·55	295·0	542·7	548·3	734·2
Velocity in cm./sec. (calculated from Allen's formula)	4·63	26·2	34·95	39·02	42·8

TABLE III.

Radius of Bubble, cm.	·025	·12	·15	·176	·19	·205	·216	·22	·247	·265	·272	·334	·351
Velocity, cm./sec.	9·85	24·5	27·5	26·75	26·5	25·5	24·85	24·5	24·3	23·75	23·5	23·35	23·0
Value of $\phi^{1/2}$	·0257	·1087	·1353	·1779	·2002	·2378	·2574	·2694	·321	·368	·3866	·5295	·5791

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formula is applicable only when the bubble is very small, and that, for the larger ones, Allen's linear formula holds somewhat approximately.

Both of these formulæ, however, show that the velocity increases without limit as the size of the bubble increases, which seems questionable from a mere common-sense point of view, and how could the existence of a maximum velocity be expected from them as shown by a curve in fig. 10? It is naturally misleading to compare a bubble with a solid sphere, and any formula deduced from the analogy of a solid sphere cannot be applied to a bubble except in the case of very small ones. The shape of a bubble is never spherical; it changes momentarily throughout its course. It is not so simple that it may be compared with a solid and be represented by a simple formula obtained from the mere analogy of a solid.

Equation of Motion.—For considering the equation of motion of an air-bubble in water the following assumptions will be made:—

(1) The volume of the bubble is constant during its motion.

(2) The bubble moves up along a vertical straight course.

The depth of water in the experiment vessel used in the present experiment being about 25 cm. and the change of volume at the surface being only 0·02 or 1/50 time of volume at the bottom, the first assumption will be justified without any sensible error. The second assumption differs somewhat from the actual motion, but it may to some extent be justified.

From a close inspection of a moving bubble we found that there always remained an upward current of water which moves after the bubble, and the larger the bubble the larger the mass of the upward current was. This is an indication that a bubble does not perfectly slip in its motion, but it carries with it a certain mass of surrounding water depending on its size.

On this consideration, and with the assumption that the resistance to motion varies as the square of the velocity, as is usual in treating of the motion of a body in a viscous fluid, we have assumed the following equation of motion, taking the axis of z upwards to be positive:—

$$\left(\sigma V + \frac{1}{k}\rho V\right)\frac{d^2z}{dt^2} = g(\rho-\sigma)V - \phi\left(\frac{dz}{dt}\right)^2, \quad . \quad . \quad (3)$$

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where σ = density of the air,
ρ = density of the water,
V = volume of the bubble,
ϕ = coefficient of resistance depending on the size of the bubble,
and k = coefficient depending also on the size of the bubble.

In this equation, $\frac{1}{k}\rho V$ is the mass of water carried up with the bubble under the assumption that it is $1/k$ times of the mass of water displaced by it and $g(\rho-\sigma)V$ is the buoyancy.

Under standard pressure and at the average temperature of 18° C., σ is as small as 0·0012 in C.G.S. units, which is negligible in comparison with ρ, and the mass of water carried up by the bubble seems to be so great that the mass of air in it is also negligible. The above equation then may be written in the form :—

$$\frac{1}{k}\rho V\frac{d^2z}{dt^2}=g\rho V-\phi\left(\frac{dz}{dt}\right)^2$$

or

$$\frac{d^2z}{dt^2}=kg-\frac{k\phi}{\rho V}\left(\frac{dz}{dt}\right)^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Putting

$$\frac{dz}{dt}=\xi \text{ and } \frac{k\phi}{\rho V}=A,$$

it gives

$$\frac{d\xi}{dt}=kg-A\xi^2,$$

or

$$dt=\frac{d\xi}{kg-A\xi^2};$$

and integrating we obtain

$$t=\frac{1}{2\sqrt{kgA}}\log\frac{\sqrt{kg}+\xi\sqrt{A}}{\sqrt{kg}-\xi\sqrt{A}}+C.$$

At the beginning of the motion when $t=0$, the velocity of the bubble ξ is zero, so that the integration constant C in the above equation is zero. Hence we have :—

$$t=\frac{1}{2\sqrt{kgA}}\log\frac{\sqrt{kg}+\xi\sqrt{A}}{\sqrt{kg}-\xi\sqrt{A}}$$

or

$$\exp(2t\sqrt{kgA})=\frac{\sqrt{kg}+\xi\sqrt{A}}{\sqrt{kg}-\xi\sqrt{A}},$$

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from which solving for ξ we get

$$\xi=\sqrt{\frac{kg}{A}}\left[1-\frac{2}{1+\exp(2t\sqrt{kgA})}\right],$$

or

$$\frac{dz}{dt}=\sqrt{\frac{g\rho V}{\phi}}\left[1-\frac{2}{1+\exp\left(2kt\sqrt{\frac{g\phi}{\rho V}}\right)}\right] \quad . \quad . \quad (5)$$

This is the expression for the velocity of the bubble with respect to the time.

Again integrating the above equation we get

$$z=\sqrt{\frac{g\rho V}{\phi}}\left\{t-2t+\frac{1}{k\sqrt{\frac{g\phi}{\rho V}}}\times\log\left[1+\exp\left(2kt\sqrt{\frac{g\phi}{\rho V}}\right)\right]\right\}+C.$$

Taking the origin at the centre of the nozzle where the motion starts, we have $z=0$ when $t=0$, and the integration constant C in the above equation is

$$C=-\sqrt{\frac{g\rho V}{\phi}}\cdot\frac{1}{k\sqrt{\frac{g\phi}{\rho V}}}\log 2,$$

and we have

$$z=-\sqrt{\frac{g\rho V}{\phi}}\,t+\frac{\rho V}{k\phi}\log\frac{1+\exp\left(2kt\sqrt{\frac{g\phi}{\rho V}}\right)}{2}. \quad (6)$$

This is the equation expressing the relation between the position and the time of a bubble.

As the terminal velocity is a constant velocity, as already said, it must be such that it is independent of t, and with reference to (5), if v be the terminal velocity, it must be

$$v=\sqrt{\frac{g\rho V}{\phi}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

and the corresponding expression for z will be

$$z=z_1+\sqrt{\frac{g\rho V}{\phi}}(t-t_1), \quad . \quad . \quad . \quad . \quad (8)$$

z_1 being the displacement at time t_1 after the terminal velocity is passed.

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If r be the radius of the bubble measured just at the moment of its leaving the nozzle, when its shape is a sphere, its volume V will be equal to $\frac{4}{3}\pi r^3$, and we have by (7):

$$\phi^{1/2} = \frac{\sqrt{g\rho V}}{v} = \sqrt{\frac{4}{3}\pi g\rho}\,\frac{r^{3/2}}{v},$$

which in C.G.S. units gives

$$\phi^{1/2} = 64{\cdot}10\frac{r^{3/2}}{v} \quad \text{or} \quad \phi = 4110\,\frac{r^3}{v^2}. \quad . \quad . \quad (9)$$

The resistance to motion of a bubble with a terminal velocity will be, therefore,

$$\text{Resistance} = \phi v^2 = 4110 r^3, \quad . \quad . \quad . \quad (10)$$

that is, the resistance is proportional to the cube of its radius or to its volume, and not to its projected area as often may be expected.

Table III. shows the value of $\phi^{1/2}$ calculated from the above equation with r and v obtained from the present experiment, and fig. 13 shows diagrammatically the relation between r and $\phi^{1/2}$, by which it can be seen how the value of $\phi^{1/2}$ increases with respect to the radius.

Equations (5) and (6) are applicable only before the terminal velocity is reached, and in that case, if z_0 be the displacement at time t_0, (6) will give

$$z_0 + \sqrt{\frac{g\rho V}{\phi}}\,t_0 = \frac{\rho V}{k\phi}\log\frac{1+\exp\left(2kt_0\sqrt{\frac{g\phi}{\rho V}}\right)}{2},$$

or putting

$$\left(z_0 + \sqrt{\frac{g\rho V}{\phi}}\,t_0\right)\frac{\phi}{\rho V} = P, \quad \text{and} \quad \sqrt{\frac{g\phi}{\rho V}}\,t_0 = Q,$$

we have

$$kP = \log\frac{1+\exp(2kQ)}{2}$$

or

$$2\exp(kP) = 1 + \exp(2kQ) \quad . \quad . \quad . \quad . \quad (11)$$

The experimental coefficient k can be determined by solving this equation, which can be accomplished most conveniently by graphical means, and in order to do this the first thing will be to calculate the values of P and Q. The values of $\phi^{1/2}$ in the expression of P and Q are given in Table III., and the question is what values are to be given

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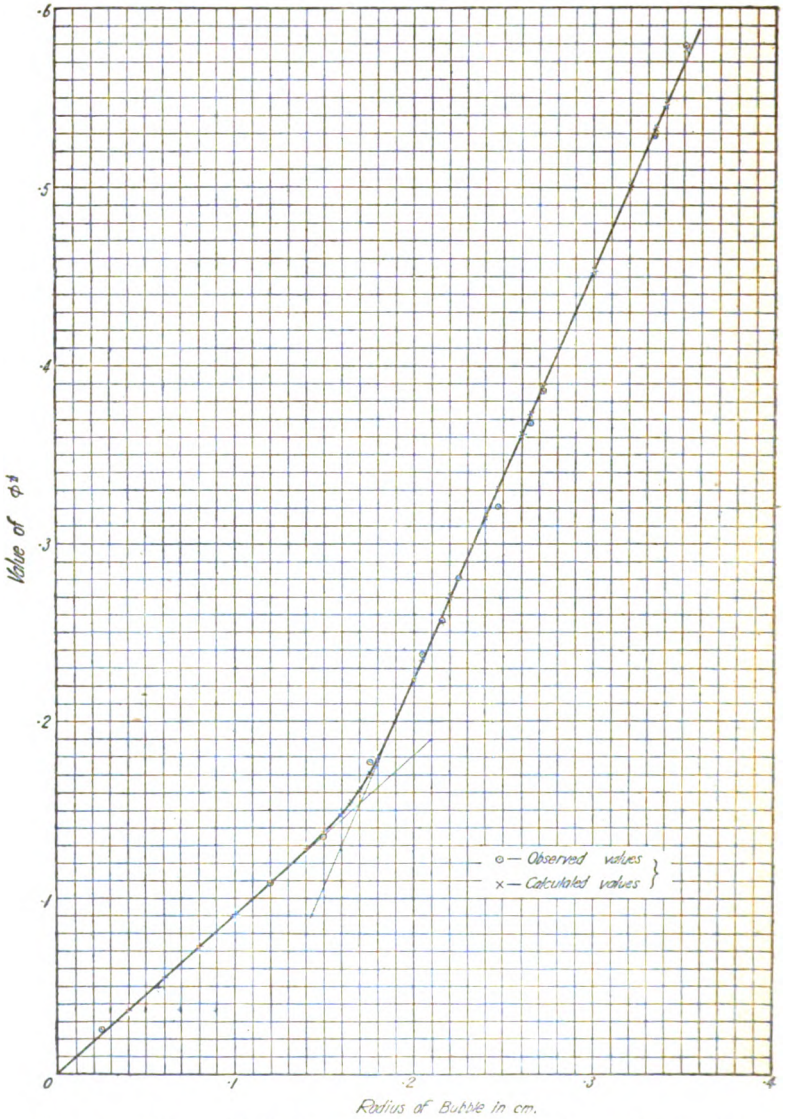
Fig. 13.



for z_0 and t_0. Strictly speaking, all the values of z_0 and t_0 must satisfy (11), if we take them in the course of time before the terminal velocity is reached. Actually, however, the bubble attains its terminal velocity almost as soon as it

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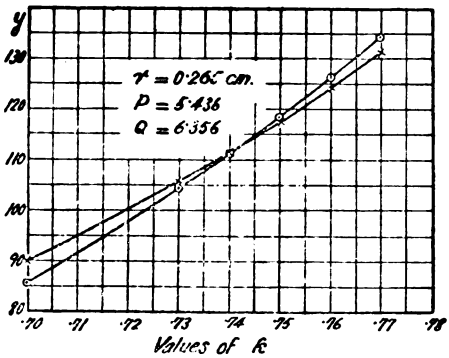
has left the nozzle, and the "critical position," that is, the position at which the terminal velocity is first attained, is very near to the nozzle, and it is difficult to find the correct values for z_0 and t_0. Here we have taken the middle point of the displacement to the critical position for z_0 and corresponding time for t_0 measured on the averaging curves, some of which are shown in figs. 5 to 9, to get rid as much as possible of the errors. The values of P and Q calculated by such procedure are given in Table IV.

How the calculated results with such values of P and Q coincide closely with the actual results can be seen in figs. 5 to 9, in which the points with circular marks are those plotted in accordance with the experiments, and those with cross marks are those calculated from (5) and (6).

The graphical solution of (11) is made by plotting two curves $y=2\exp(k\rho)$ and $y=1+\exp(2k\mathrm{Q})$ for various values of k with given values of P and Q. The value of k read at the intersection of these curves is the value of k to be found which satisfies (11). Figs. 14 and 15 show only two of such

Fig. 14.



solutions applied as examples to the bubbles of the radii of 0·265 cm. and 0·351 cm. In Table V. the values in the third column give the values of k obtained by such graphical solutions.

In the fourth column in Table V. the values of kr^2 are given, by which we can see at a glance that kr^2 is approximately constant, irrespective of the size of the bubbles, the mean value of it being 0·054. We have, therefore,

$$kr^2 = \text{constant} = 0{\cdot}054 \quad . \quad . \quad . \quad . \quad . \quad (12)$$

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Fig. 15.

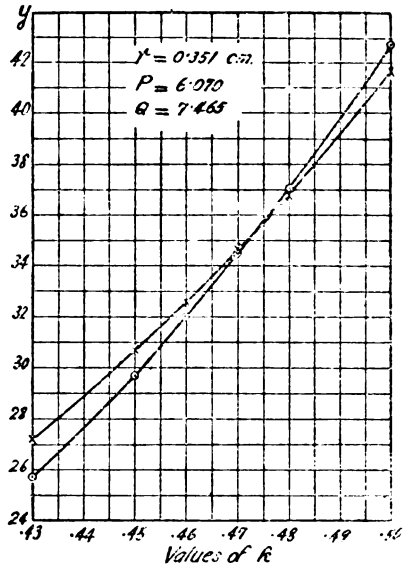

TABLE IV.

Radius of Bubble. cm.	z_0. cm.	t_0. sec.	Value of P.	Value of Q.
·12	1·25	·0556	4·267	4·451
·15	1·35	·0570	3·779	4·060
·176	1·35	·0611	4·088	4·478
·19	1·33	·0618	4·140	4·567
·205	1·33	·0663	4·553	5·096
·216	1·30	·0673	4·718	5·310
·265	1·30	·0770	5·436	6·356
·272	1·34	·0824	5·813	6·871
·334	1·30	·0872	5·996	7·320
·351	1·262	·0876	6·070	7·465

The last column in Table V. shows the values of k calculated from this equation, and fig. 16 shows the points plotted according to the third and the last columns in Table V., by which their close coincidence can be seen.

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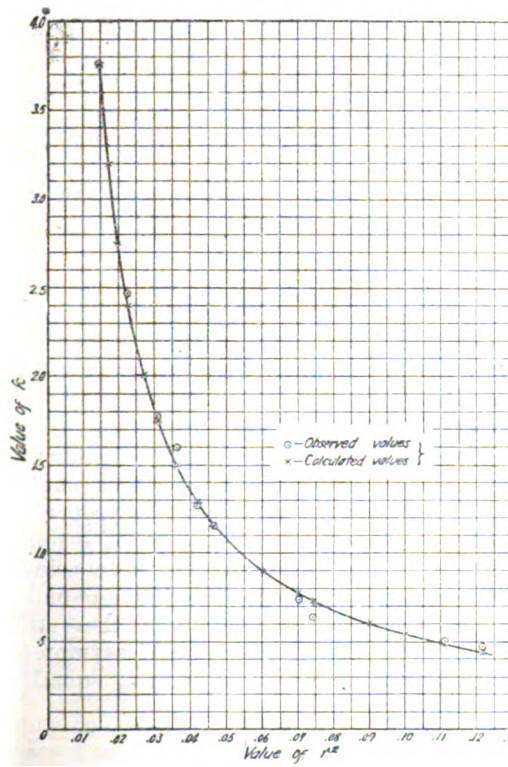
TABLE V.

Radius of Bubble. r cm.	Value of r^2.	Value of k (observed).	Value of kr^2.	Value of k (calculated).
·12	·0144	3·76	·05414	3·75
·15	·0255	2·47	·05558	2·40
·176	·0310	1·78	·05514	1·74
·19	·0361	1·60	·05776	1·50
·205	·0420	1·27	·05337	1·285
·216	·0467	1·165	·05435	1·16
·265	·0702	·74	·05197	·7695
·272	·0740	·64	·04735	730
·334	·1116	·505	·05634	·785
·351	·1232	·47	·05790	·439

Fig. 16.



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The physical meaning of kr^2=constant is that the percentage mass of water carried up with a bubble is proportional to the square of its radius or to its surface area.

Terminal Velocity.—Referring to fig. 13 we may see that the points of $\phi^{1/2}$ plotted against r are distributed approximately on the two kinds of straight lines intersecting at the point of about $r=0{\cdot}17$ cm. and $\phi^{1/2}=0{\cdot}154$. This indicates that there are two kinds of motion of bubbles which are governed by the different proportional resistance, and the resistance almost suddenly increases to a larger proportion at the "critical radius," which is the radius of the bubble at which the above two straight lines intersect. According to the present experiment the critical radius is, therefore, about 0·17 cm.

From the analogy of the stream-line and turbulent motions of the flow of fluid which are distinguished by the critical velocity, we may conclude that in the case of a moving bubble a kind of turbulent motion suddenly takes place in the space surrounding the bubble, when the bubble is equal to the critical radius, and that it makes its shape and passage unstable to make it display a greater rate of resistance. This fact can be clearly understood by examining the shapes and passages of the bubble in the photographs. It follows, therefore, that the velocity will be a maximum for a bubble of critical radius.

According to the method of least squares the equations of the above two straight lines are :

$$\phi^{1/2}=0{\cdot}9055\,r$$

and

$$\phi^{1/2}=2{\cdot}305\,r-0{\cdot}2374,$$

the inclinations to the axis of r being 42° 10′ and 66° 33′ respectively, and the coordinates of the point of intersection being $r=0{\cdot}17$ and $\phi^{1/2}=0{\cdot}154$.

With reference to fig. 10 we cannot discover any discontinuity on the curve of v against r. It follows, therefore, that on the curve of $\phi^{1/2}$ against r there must not be a perfect discontinuity. Hence, in fig. 13, it is proper to see the curve as one continuous curve instead of seeing it as the combination of two straight lines. On this consideration and also for mathematical convenience, we have assumed it to be a hyperbola of the second order which has these straight lines as its asymptotes. Then, with these asymptotes as the oblique coordinate axes X and Y, the equation of the hyperbola has been found to be

$$XY=0{\cdot}000108,$$

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from which the following formula has been deduced :

$$\phi+(0{\cdot}236-3{\cdot}2r)\phi^{1/2}+(2{\cdot}07r^2-0{\cdot}211r-0{\cdot}000282)=0 \quad (13)$$

and solving $\phi^{1/2}$ from this we have

$$\phi^{1/2}=1{\cdot}6r-0{\cdot}118+\sqrt{0{\cdot}49r^2-0{\cdot}167r+0{\cdot}0142}. \quad (14)$$

Table VI. shows the values of $\phi^{1/2}$ calculated from this formula against their observed ones given in Table III., and fig. 13 shows these plotted on a diagram, by which their close coincidence can be seen.

With calculated values of $\phi^{1/2}$ the terminal velocities can be determined by (9). In order to obtain a formula for the terminal velocity, substitute $\phi^{1/2}$ given in (9) in (13), then the following will result :

$$(2{\cdot}07r^2-0{\cdot}211r-0{\cdot}000282)v^2 \\ +(15{\cdot}1-205r)r^{3/2}v+4110r^3=0 \quad . \quad . \quad . \quad (15)$$

The terminal velocity of a bubble whose radius is r can be solved from this quadratic equation. Table VII. shows those calculated against their observed ones given in Table I. and those plotted on a diagram are shown in fig. 10, by which it can also be seen how they coincide closely.

From our formulæ deduced above we can find the following facts :—

(1) When the bubble is so small that Stokes' formula may be applied, the terms containing r in (14) become negligible and $\phi^{1/2}$ becomes constant. It follows that when the bubble is very small the terminal velocity v varies as $r^{3/2}$ as is obvious from (9). This does not agree with Stokes' formula (1), but as the present experiment was not carried out on such small bubbles, owing to the difficulty of making them, our formulæ cannot be compared with Stokes' to find how the former is approximated to the latter.

(2) When the bubble is smaller than about 0·04 cm. in radius as Mr. Allen treated in his experiment, the first term in the right-hand side of (14) is negligible in comparison with the second, and the term with r^2 in the square-root sign is also negligible in comparison with the accompanying two terms. It follows, therefore, that in this case $\phi^{1/2}$ varies according to the square root of r, other terms being all constant values, and that the terminal velocity varies linearly as the radius, as is evident from (9). Hence our formula is perfectly coincident with Allen's formula (2), so that the former may be considered to include the latter, which may be considered to be only a special case of the former.

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TABLE VI.

Radius r cm.	·025	·04	·06	·08	·1	·12	·14	·15	·16	·165	·176	·18	·19	·2
Value of $\phi^{1/2}$ (observed)	·0257	—	—	—	—	·1087	—	·1353	—	—	·1779	—	·2002	—
Value of $\phi^{1/2}$ (calculated)	·0237	·0372	·0553	·0734	·0915	·1096	·128	·136	·148	·1546	·1725	·18	·202	·224
Radius r cm.	·205	·216	·22	·24	·247	·26	·265	·272	·28	·3	·32	·334	·351	
Value of $\phi^{1/2}$ (observed)	·2378	·2574	·2694	—	·321	—	·368	·3866	—	—	—	·5295	·5791	
Value of $\phi^{1/2}$ (calculated)	·2357	·261	·2698	·3156	·331	·361	·3729	·389	·406	·453	·499	·531	·5766	

TABLE VII.

Radius of Bubble, cm.	·025	·12	·15	·176	·19	·205	·216	·22	·247	·265	·272	·334	·351
Velocity, cm./sec. (observed)	9·85	24·5	27·5	26·75	26·5	25·5	24·85	24·5	24·3	23·75	23·5	23·35	23·0
Velocity, cm./sec. (calculated)	10·68	24·25	27·37	27·26	26·27	25·22	24·57	24·48	23·72	23·44	23·36	23·37	23·1

(3) When the size of the bubble lies between about 0·17 cm. and 0·25 cm. in radius, the value with the square-root sign in (14) becomes negligible compared with the others,

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and it follows that $\phi^{1/2}$ varies linearly as r. Hence we find from (9) that in this case the terminal velocity varies as the square root of the radius, the curve of v against r being a parabola as seen in fig. 10.

VIII. Boundary Effect of the Experiment Vessel.

In order to get as fine and sharp photographs of the bubbles as possible, in the above experiments we used a comparatively thin experiment vessel which might give a certain boundary effect to the motion of the bubbles, especially for large bubbles.

To test this, we carried some experiments with a larger experiment vessel of the cross-section of about 15·6 cm. into 10·95 cm., set the shorter side parallel to the flash-light direction, and about 48·5 cm. high with water about 23 cm. deep.

The photographs of the bubbles were not so sharp and fine as those obtained with the thin experiment vessel, and the size of the bubbles, especially of the small ones, could not be measured so accurately as in the thin one. The results obtained, therefore, did not have much value in treating its equation of motion, but we ascertained after experiments with six different sizes of bubbles that the terminal velocities were about 4 per cent. greater for all the bubbles of practical sizes.

IX. Summary.

As the result of the present experiments we have arrived at the following conclusions:—

(1) When an air bubble rises from rest in still water it attains a constant terminal velocity almost as soon as it has started. (The critical position at which the terminal velocity is attained is about 3 to 4 cm. high above the air-nozzle.)

(2) The terminal velocity is maximum for a bubble whose radius is equal to the critical radius. (The critical radius is about 0·165 cm. and its terminal velocity is about 27·8 cm. per sec.)

(3) For bubbles smaller than the critical radius the terminal velocities increase approximately linearly with their sizes.

(4) For bubbles larger than the critical radius the terminal velocities decrease nearly parabolic with the sizes, and

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tend to be constant irrespective of their sizes. (The constant velocity is about 23 cm. per sec.)

(5) The rate of resistance almost suddenly increases at the critical radius, and the shape and the course of the bubble become unstable at it.

(6) The bubble traces a kind of a helical course on its upward motion and it displays a flattened outline, the major axis of which lies perpendicular to its course.

(7) The ratio of the mass of water carried up with a passing bubble to that displaced by it is proportional to the square of its radius or to its surface area.

(8) The resistance to motion of a bubble is proportional to the cube of its radius or to its volume.

(9) The following equation of motion agrees closely with the practical case, with the axis of z upwardly directed.

$$\frac{1}{k}\rho \mathrm{V}\frac{d^2z}{dt^2}=g\rho\mathrm{V}-\phi\left(\frac{dz}{dt}\right)^2,$$

where ρ = density of the water,
V = volume of the bubble,
ϕ = coefficient of resistance depending on the size of the bubble,
and k = coefficient depending also on the size of the bubble.

The values of ϕ and k should be calculated from the following empirical formulæ :—

$$\phi=(1{\cdot}6r-0{\cdot}118+\sqrt{0{\cdot}49r^2-0{\cdot}167r+0{\cdot}0142})^2,$$

and $$k=\frac{0{\cdot}054}{r^2},$$

r being the radius of the bubble as measured just at the moment of its leaving the nozzle when it shows a spherical outline. All are expressed in C.G.S. units.

(10) The terminal velocity v in cm. per sec. of a bubble the radius of which is r cm. is determined by solving the following quadratic equation :

$$(2{\cdot}07r^2-0{\cdot}211r-0{\cdot}000282)v^2+(15{\cdot}1-205r)r^{3/2}v+4110r^3=0.$$

(11) The above results contain the very slight boundary effect of the experiment vessel by which the terminal velocity in a widely open space is about 4 per cent. greater than that obtained above.

Sendai, Japan.
July 8, 1924.

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XI. *On a Method of Calculating the Vapour Pressure of a Solution with a Simple Solvent and a Non-Volatile Solute.* *By* SASI BHUSHAN MALI *.

IN the theoretical calculation of the constant of integration of the vapour pressure formula for a substance from kinetic considerations, Stern † makes use of a simple mechanical model. He assumes that inside the body of the substance there are points P, such that they attract the molecules with forces proportional to the distance r of the individual molecules from each of the points in question. The work done by a molecule in freeing itself from the influence of such a point is, according to Stern, the latent heat of evaporation of that molecule. The forces of attraction due to the points P which operate on the molecule are of such a nature that they vanish beyond a certain distance s from the points P, which are supposed to be surrounded by spherical spheres of influence. Within the sphere of influence the molecules (or rather atoms) vibrate as monochromatic resonators, while in the rest of the space surrounding these spheres of influence they fly about like ordinary gas molecules. Hence, the potential energy of the individual molecules at every point in space is fixed. Here, Stern makes use of Boltzmann's law of logarithmic distribution to determine the ratio of the density of the molecules inside the spheres of influence, and also in the free space intervening between these spheres, and he makes the further important assumption that inside each sphere of influence there is only one vibrating atom. The vapour pressure of the substance can now be uniquely determined if we remember that, according to Stern's model, there are as many attracting centres P in a substance as there are atoms in the substance.

The working model of Stern essentially resembles the known model of matter in the crystalline state as revealed by X-ray work, for in crystals the atoms are vibrating about positions of rest. And in fact Stern's value for the integration constant actually coincides with those found by Sackur ‡ and Tetrode § for monatomic vapours. This is especially noteworthy in view of the fact that some physicists of the

* Communicated by Prof. W. A. Jenkins, M.Sc., I.E.S.

† Stern, *Physik. Zeitschr.* xiv. p. 629 (1913). Also Nernst's 'Theoretischen und experimentellen Grundlagen des neuen Wärmesatze,' 1918 edition, p. 138.

‡ Sackur, *Ann. d. Phys.* xl. p. 67 (1913).

§ Tetrode, *Ann. d. Phys.* xxxviii. p. 434; xxxix. p. 255 (1912).

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present day * are inclined to believe that matter in the liquid state possesses an unstable crystalline structure.

Stern has determined the vapour pressure formula for simple condensed systems. It appears that with very simple modifications his assumptions can be utilized to find the vapour pressure formula for a dilute solution with a non-volatile solute, especially when the solvent is monatomic both in the liquid and in the vapour state. A solution consists of a certain distribution of solvent molecules with a rarer distribution of solute molecules superimposed upon the former. On account of the mutual attraction of the solute molecules and the surrounding solvent molecules, the distribution of the solvent molecules just around a solute molecule will be somewhat different from the distribution at points further away from the solute molecules.

And owing to the presence of the solute molecules the general distribution of the solvent molecules at points beyond the immediate influence of the solute molecules will be somewhat different from that in the pure solvent, and this even though the amount of solvent in a certain volume may remain the same in the pure state as well as in the state of solution. We shall now make use of Stern's reasoning in order to develop a vapour pressure formula for the solution. If, in the pure state, n_0 and ϕ_0 respectively denote the molecular density and the potential energy of a molecule in free space, and if n_r and ϕ_r denote the same quantities at a point inside a sphere of influence whose distance from the corresponding equilibrium point P is r, then, according to Boltzmann's law,

$$n_r/n_0 = e^{-\frac{\phi_r}{kT}}/e^{-\frac{\phi_0}{kT}}.$$

In the corresponding case of the solution the value of n_r remains unchanged, since the volume of the solvent molecule is supposed to be unaffected by the presence of the solute molecule. The value of ϕ_0 is, however, increased by an amount proportional to the number of solute molecules in unit volume of the solution, and the molecular latent heat in free space of the solution may be expressed as $\phi_0 + cn$ †,

* Debye and Scherrer, *Nachr. Kgl. Ges. Wiss. Göttingen*, 1916; Eastman, J. A. C. S. xlvi. p. 917 (1924).

† ϕ_0 is the latent heat of evaporation of a solvent molecule from the pure solvent, and $\phi_0 + cn$ is that of the same molecule from the solution. Hence, cn is the heat of dilution of the solution, and is defined by Sackur (Sackur's 'Thermo-chemistry and Thermo-dynamics,' 1917 ed. p. 228) as "the amount of heat evolved when a large volume of the liquid is diluted by the addition of one molecule of the solvent."

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where c is a constant and n is the number of solute molecules in one c.c. of the solution. We do not know in what way n_0 and ϕ_r will change in the case of the solution, but we can at once determine their product by the application of Boltzmann's law of distribution. Thus, in the case of the solution

$$n_r = n_0 e^{-\frac{\phi_r}{kT}} . e^{\frac{\phi_0 + cn}{kT}}.$$

But, since there is only one molecule (or atom) in the sphere of influence,

$$1 = \int_0^s n_r . 4\pi r^2 dr = n_0 e^{\frac{\phi_0 + cn}{kT}} . 4\pi \int_0^s e^{-\frac{\phi_r}{kT}} r^2 dr.$$

The force acting on the molecule vibrating inside the sphere of influence is represented by the equation

$$m\frac{d^2r}{dt^2} + a^2 r = 0.$$

The potential energy ϕ_r of a vibrating molecule when at a distance r from an attracting centre P is equal to $\frac{a^2r^2}{2}$, and the potential energy $\phi_0 + cn$ in free space is equal to $\frac{a^2s^2}{2} + cn$. Thus, we find

$$\int_0^s e^{-\frac{\phi_r}{kT}} r^2 dr = \int_0^s e^{-\frac{a^2r^2}{2kT}} r^2 dr.$$

To simplify the right-hand side of the equation we may put

$$\frac{a^2r^2}{2kT} = x^2, \quad \text{and} \quad \frac{a^2s^2}{2kT} = x_0^2.$$

Then,

$$\int_0^s e^{-\frac{a^2r^2}{2kT}} r^2 dr = \left(\frac{kT}{a^2/2}\right)^{3/2} \int_0^{x_0} e^{-x^2} x^2 dx.$$

If λ_0 denotes the latent heat of evaporation of the solvent when the solute is absent, $x_0^2 = \frac{\lambda_0}{RT}$, and this must be a large number compared with unity, for $\frac{\lambda_0}{T}$ represents the Trouton constant, and its value is of the order of 21 at the boiling

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point of normal liquids and has higher values at temperatures lower than the boiling points *, whereas R has the value 2. Hence, $e^{-x_0^2}$ must be a very small quantity. Thus, in the integration of the equation $\int_0^{x_0} e^{-x^2} x^2 dx$ we may, without appreciable error, take the upper limit of the integration to be ∞ instead of x_0. Integrating the equation in this way, according to Nernst's "Rekursion Formel," Stern shows that

$$\int_0^{x_0} e^{-x^2} x^2 dx = \frac{\sqrt{\pi}}{4}.$$

In this way we finally get

$$1 = n_0 e^{\frac{\phi_0 + cn}{kT}} . \pi^{3/2} \left(\frac{kT}{a^2/2}\right)^{3/2},$$

$$\text{or} \qquad n_0 = e^{-\frac{\phi_0 + cn}{kT}} . \left(\frac{a^2/2}{\pi kT}\right)^{3/2}.$$

Substituting $m(2\pi\nu)^2$ for a^2

$$n_0 = e^{-\frac{\phi_0 + cn}{kT}} . \left(\frac{2\pi m\nu^2}{kT}\right)^{3/2}.$$

Now, in a dilute solution, we may suppose that most of the solvent molecules are distributed at points beyond the influence of the solute molecules and have a distribution of n_0 molecules per unit volume. Hence, in the case of a dilute solution, we may put

$$p = n_0 kT = e^{-\frac{\phi_0 + cn}{kT}} . \frac{(2\pi m\nu^2)^{3/2}}{(kT)^{1/2}},$$

$$\text{or} \quad \ln p = \frac{\phi_0 + cn}{kT} - 0{\cdot}5 \ln T + \ln \frac{(2\pi m)^{3/2}\nu^3}{k^{1/2}}.$$

If λ_0' denotes the latent heat of evaporation of a gram mol. of the solvent from the solution

$$\ln p = -\frac{\lambda_0'}{kT} - 0{\cdot}5 \ln T + \ln \frac{(2\pi m)^{3/2}\nu^3}{k^{1/2}} . \quad . \quad , \quad (1)$$

Also, for the pure solvent, Stern has shown that

$$\ln p_0 = -\frac{\lambda_0}{kT} - 0{\cdot}5 \ln T + \ln \frac{(2\pi m)^{3/2}\nu^3}{k^{1/2}} . \quad . \quad . \quad (2)$$

* Mali, Phil. Mag. xlv. p. 94 (1923).

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We thus find that the vapour pressure formulæ for the pure solvent and the solution with a non-volatile solute differ only in the terms containing the latent heat of evaporation, but are otherwise identical. And specially we notice that the constant of integration comes out as identical in both the cases. This is as is to be expected, for the constant of integration, as explained by Nernst, depends upon the nature of the evaporating molecules and is independent of the nature of the condensed system.

There are certain consequences to be derived from these results. From equations (1) and (2)

$$\ln\frac{p_0}{p} = \frac{cn}{kT},$$

and since p_0 and p are approximately equal,

$$\ln\frac{p_0}{p} = \frac{p_0-p}{p} = \frac{p_0-p}{p_0} \text{ approximately.}$$

Thus, the lowering of the vapour pressure of the solution is proportional to the concentration of the solute. Again, from thermodynamics,

$$\frac{p_0-p}{p_0} = \frac{\lambda_0 dT}{RT_0^2},$$

where dT is the raising of the boiling point corresponding to the lowering of the pressure by the amount p_0-p. Combining these two equations, we find that

$$Ncn = \frac{\lambda_0 dT}{T} \text{ approximately.}$$

Or, Heat of dilution of the solution = Heat of evaporation $\times \frac{dT}{T}$, where dT is the difference in boiling points of the original and the dilute solutions.

The present arguments may not be strictly accurate in the case of metals, for the metals are monatomic in the vapour state, yet from surface tension data they are found to be associated in the liquid state (Siedentopf, *Wied. Ann.* lxi. p. 265 (1897). These arguments will be strictly true in the case of a hypothetical liquid which is monatomic both in the liquid and in the vapour state.

Finally, I have to record my thanks to Prof. W. A. Jenkins for the kind interest he took in the work during the course of its progress.

Department of Physics,
University of Dacca.
Sept. 7, 1924.

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XII. *The Temperature Dependency of the Molecular Heats of Gases, especially of Ammonia, Methane, and Hydrogen, at Low Temperatures.* By FRANKLIN A. GIACOMINI, *M.A., Ph.D.**

[Abridged Report.]

SINCE the discovery of the extraordinarily rapid fall of C_v for hydrogen down to the value of a monatomic gas at low temperatures (first observed by Eucken), physicists have been endeavouring to explain this phenomenon (which seems to stand in marked opposition to the deductions of the Equipartition of Energy Theorem) chiefly by means of the Quantum Theory †. None of the attempts made thus far, however, have been successful, and until a greater body of empirical evidence has been obtained with regard to the behaviour of the molecular heats of gases at low temperatures, little hope can be entertained of making any positive progress in this direction ‡. The work outlined in this paper was undertaken for the purpose of providing additional data concerning the relation of the energy-content of gas molecules to the temperature,—particularly in that temperature-domain in which the value of the said energy-content sinks beneath that value which the molecule must have when considered as perfectly rigid and as having three degrees of freedom of rotation (decrease in the rotational energy of the molecule).

* Communicated by Prof. J. R. Partington.

† It is of interest to note that, previous to Eucken's observations, Nernst had predicted the rapid fall of C_v for H_2 with decreasing temperatures as a necessary consequence of his thermo-dynamical theorem by applying the Quantum Theory to gases; Eucken's experiments were subsequently made to test the correctness of this deduction of Nernst.

‡ Among the many theoretical attempts made, which (in addition to the theories of Planck-Einstein and of Nernst-Lindemann, both of which had previously been developed for the purpose of accounting for the decrease of the vibrational energies of the atoms in solids, by diminishing temperature) have been built up for the sole purpose of explaining the decrease of the rotational energies of gas molecules by falling temperature, may be mentioned the following:—Planck. *Berichte d. deutsch. Phys. Gesellsch.* li. p. 285 (1915), which is founded on the assumption of coherent degrees of freedom of the molecules; S. Rotszayn, *Ann. d. Phys.* lvii. p. 81 (1918), which assumes incoherent degrees of freedom between the molecules; and in addition to these:—

E. Holm, *Ann. d. Phys.* xlii. p. 1311 (1913); Ehrenfest, *Verhandl. d. deutsch. Phys. Gesellsch.* xv. p. 451 (1913); A. Einstein und O. Stern, *Ann. d. Phys.* xl. p. 551 (1913); v. Wyssenhof, *Ann. d. Phys.* li. p. 285 (1916); F. Reiche, *Ann. d. Phys.* lviii. p. 657 (1919); G. W. Todd, Phil. Mag. xl. p. 357 (1920) (based on the Classical Theory).

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By so doing a system of data is obtained for the study of the molecular energies which is reduced to its utmost simplicity. The plan of the work decided upon, therefore, involved the following objectives :—

(1) The determining upon and the examining of all such gases (chiefly those having small molecular moments of inertia) which in addition to hydrogen might, in all probability, still show an experimentally establishable decrease in their molecular energy-content, C_v, by falling temperatures, below the C_v-values corresponding to rigid molecules (decrease in the rotational energy of the molecule).

(2) The determining, as far as possible, of the specific-heat-temperature curves (C_v-T-Curves) for these gases.

As a prerequisite to the attaining of this end there was necessary :—

(3) The developing of a method by means of which the molecular energy-content, C_v, can be *directly* obtained, *i. e.* determined, as far as possible, without the use of any assumptions or hypotheses concerning either the ratio of the specific heats, C_p/C_v, at the temperatures in question or the other thermodynamical corrections usually necessary to reduce the observed values of C_v to their true values at low temperatures.

The method used, however, requires that the gas under investigation be as nearly as possible in the ideal state (measurements at small gas pressures, see below). This follows, first, as a consequence of the fact that, in the measurements, the coefficient of pressure-increase of the gas $(dp/dT)_v$, is assumed to be approximately that of an ideal gas and to be practically independent of the temperature, *i. e.*, that $(d^2p/dT^2)_v=0$ (*vide* Principle of the Method, below) ; and, secondly, from the desirability of avoiding, as far as possible, the corrections needed to reduce the obtained values of C_v to the values C_v would have if the gas were in the ideal state, *i. e.*, for $p=0$. This second condition is also fulfilled when $(d^2p/dT^2)_v=0$, as is evident from the general thermodynamical relation

$$(dC_v/dv)_T=T \cdot (d^2p/dT^2)_v.$$

No claims are made for the applicability of this method to measurements of precision on the absolute values of C_v. *The scope of the method is essentially the enabling of qualitatively accurate determinations of the relative values of* C_v *for the same gas over a large range of temperature (downward) and of the relative values of* C_v *for various gases at the same temperature and pressure.*

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Principle of the Method.

The method, which was adopted as the result of a suggestion of Professor Nernst, to whom I here wish to express my sincere thanks, depends on the principle, first enunciated by Nernst, concerning the determinability of the molecular heat of a gas at constant volume,—even when the heat increment added to a given volume of the gas is not uniformly distributed throughout the gas but is isolated in heat-zones or clouds in the interior of the containing-vessel (avoidance of heat-conduction directly to the walls of the containing-vessel). The comparison-measurements of C_v are obtained by determining with a very sensitive membrane-galvanometer the pressure rise which immediately follows upon the transmission of a small inductive electrical impulse through a diminutive constantan foil placed towards the centre of the vessel (*vide* Apparatus). This method of determining C_v was first tried out by Voller *. He limited his trials, however, to room temperature and atmospheric pressure. No investigation was then (or has since been) made concerning the validity of this principle of determining C_v; nor concerning the conditions that must be fulfilled if the principle be at all allowable in order to obtain reliable results.

The first matter to be settled in these researches was, accordingly, (*a*) to examine whether, or to what extent, the above described principle of determining C_v is permissible—for this principle presupposes a non-uniform temperature distribution in the gas-filling of the heating-chamber which is alone sufficient to preclude any *prima facie* assumption concerning the determinability of C_v by this principle,—and (*b*), if permissible, the establishing of the conditions under which the principle can be applied in order that reliable results may be obtainable; *i.e.*, so that C_v, and not some polytropic specific heat lying somewhere between C_p and C_v, be obtained. This question was settled:—

(1) Through an experimental investigation of what was going on in the interior of the heating-chamber immediately succeeding the induction-impulse in the heating-foil. This included the direct observation of the development and evolution of the heat-clouds in the heating-chamber (gas made visible by smoke particles); the measurement of the time required for the foil to give off its heat; the determination of the temperature attained by the foil during an

* Voller, Berlin Dissertation, 1908.

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induction-impulse; and, most important of all, the determining of the pressure-increase curves for various gases by various heat charges and under various initial conditions of pressure, etc. (see fig. 2); and

(2) Through the theoretical considerations suggested by Dr. K. Bennewitz, of the University of Berlin, concerning the thermodynamical stages gone through in the gas-filling in the interior of the heating-chamber during and immediately after the inductive impulse in the heating-foil. The fundamental idea underlying the theory of Bennewitz is this: it considers what actually takes place in the heating-chamber as identical with the following two idealized stages: (1) an isochoric heating of a small volume of the gas immediately surrounding the heating-foil, and (2) the adiabatic expansion of this volume and the adiabatic compression of the remaining part of the volume of the heating-chamber (a fuller account will be given in another paper).

As the result of the above-mentioned experimental and theoretical investigations, the conditions were ascertained which must be fulfilled in order that C_v may actually be determined. Among other things, in order to obtain reliable results, the most important condition that must be fulfilled is given by the expression

$$\left[\frac{RQ}{V_0 C_v P_0}\right]^2 << 1$$

(where Q designates the heat-charge given off by the induction-impulse; V_0, the volume of the heating-chamber; P_0, the initial pressure in the heating-chamber; C_v, the molecular heat; and R, the universal gas-constant, all expressed in absolute units). The above condition demands that for given values of V_0 and of P_0 the smallest possible value of Q be used. The expression shows, moreover, that the smaller P_0 is taken the more unfavourable the experimental conditions become; *i. e.*, the greater are the demands made on the experimental efficiency of the apparatus.

Apparatus.

The apparatus finally used (fig. 1) consisted essentially of a cylindrical metallic vessel of about 8 cm. diameter and 20 cm. height. This could easily be dipped into a Dewar vessel. The cylinder was divided into two chambers, a

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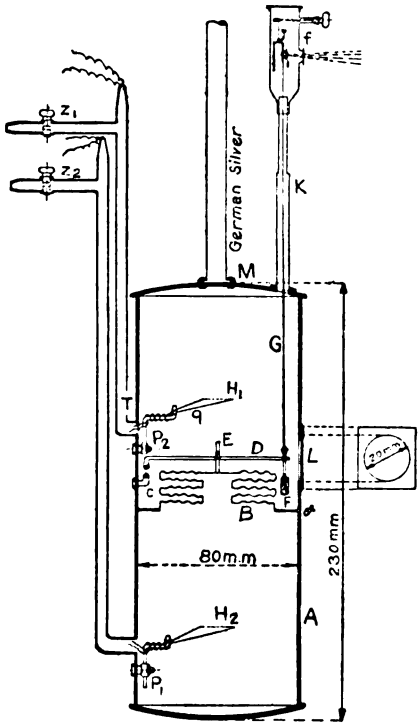
higher and a lower one. In the lower chamber (heating-chamber) of about 600 c.c. capacity there was placed the heating-foil of constantan, a metal with a negligibly small temperature coefficient of electrical conductivity. Platinum is, on account of its great temperature coefficient, not suited to comparison-measurements of C_v for various gases, or for the same gas at various temperatures. This is chiefly a

Fig. 1.



Double-heating chamber apparatus.

consequence of the discrepancies in the magnitudes of k, η *, and C_v (*i. e.*, in the heat-receiving capacity) in the two gases being compared, which causes unequal temperature variations and, therefore, unequal inductive charges in the heating-foil in the respective gas-fillings of the heating-chamber. In the higher chamber (manometer chamber) of about 300 c.c.

* k=coefficient of thermal conductivity of the gas, η=coefficient of internal friction of the gas.

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capacity was built the membrane manometer (B) with its connexions to the very sensitive deflexion mirror above, which was suspended on a cocoon fibre. The nature and magnitude of the manometer deflexions were usually observed directly by means of a telescope and scale. In the figure shown here (double-heating-chamber apparatus), the manometer chamber is of the same capacity as the lower one, and is also equipped with a heating-foil (H_1) by means of which this chamber can likewise be used as a heating-chamber simultaneously with the lower one: differential or zero deflexion method of procedure (rejected later as unsatisfactory, see below). A complete description of the apparatus will be given in another paper.

Measurements.

On account of the great difficulty in determining the absolute values of the heat charges, Q, developed by each induction-impulse, the measurements were limited to determining the relative magnitudes of the pressure-increments Δp (of the magnitude of about 0·0894 g./cm.^{2}) produced by inductive impulses of invariable magnitude in the several gases compared with that brought about in a standard gas, viz., air. The relative value, of C_v for the different gases in terms of the C_v-value for air should hereby be obtained (comparison-measurements). The value of 4·979 cal./mol . T, determined by Scheel and Heuse, was taken as the standard C_v-value for air at 291° abs. and atmospheric pressure. The relative pressure-increments were obtained by observing the relative magnitudes of the maximum manometer deflexions for the various gases under the above conditions (the corresponding mean value of ΔT in the air was 0°·025 C.). *It is very important to state here that comparisons of the maxima of the deflexions were made only when each deflexion-maximum remained at a constant and invariable value for an extended interval of time, sometimes lasting for seconds* (fig. 2). That these long-enduring pressure maxima were not spurious ones is shown by the fact that, within broad limits, the same maxima were obtained by gas-fillings (of the same gas) at different densities. A special study was made of these pressure maxima (of incredibly long duration). This will be treated of in another paper.

For the purpose of additional orientation concerning the reliability of the results obtained, a determination of the

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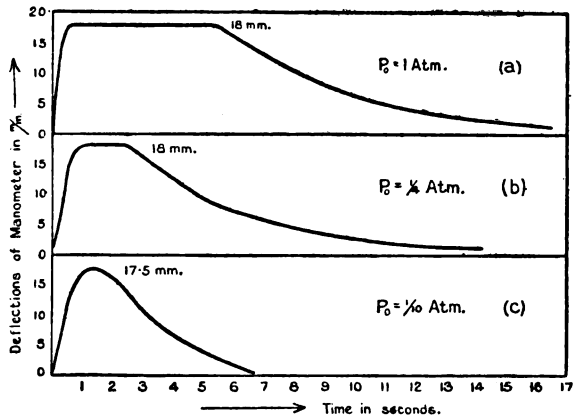
absolute value of C_v for air was attempted *. The trials showed that, although approximately correct values of C_v were obtained, the method must be further perfected before satisfactory measurements of this nature can be hoped for.

Preliminary experiments by means of a double-heating-chamber apparatus (mentioned above) were made. By this differential procedure inductive impulses are sent simultaneously into both chambers. The trials were, however, on account of the differences in phase in the pressure rise in the

Fig. 2.



The above curves (fig. 2) show the Time-Pressure-increase relations for a CO_2-gas-filling at room temperature (T = 291°) and at the indicated initial pressures, P_0, of 1, ½, and 1/10 Atmospheres.

The magnitudes of the maxima of the deflexions remain unchanged down to almost 1/10 of an atmosphere initial pressure. This fact insures us that the maxima obtained are not spurious. The duration of the maxima, however, diminishes with the decrease of the initial pressures, P_0, in the heating-chamber.

One mm. deflexion in the above curves is equivalent to about 0·0036 g./cm.^{2} pressure increment.

(two) gases being compared (caused chiefly by the discrepancies in the values of k and η of the respective gases), given up as unreliable ; therefore the first-mentioned single-heating-chamber apparatus — with successive fillings of different gases—was used in the final measurements.

* Here the determination of the magnitude of the heat-charge Q was necessary.

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The number of mols of the various gases in the heating-chamber at each gas-filling was kept practically equal by introducing the pure gas into the chamber at relatively low pressures and at room temperatures. The experiments revealed, however, that the actual number of mols of gas in the heating-chamber had very little effect on the maximum of the pressure-increments (and correspondingly deduced, values of C_v) caused by a given induction-charge; for, within broad limits of variation of the initial pressure, the maxima of the manometer deflexions remained unchanged*; or at least the variations in the pressure-increments were too small to be observable. Only for great diminutions of the initial pressure did the pressure-increments begin to decrease. This was attributed chiefly to imperfections in the apparatus, or rather to the fact that the experimental limits of the apparatus were overstepped; for the smaller the initial pressure, P_0, of the gas the greater the demands made on the efficiency of the apparatus become. All this is to be seen from the pressure-increment curves for various initial pressures spoken of above.

Two sources of error of fundamental importance, which had to be corrected for, were the following:—(*a*) the influence of the initial gas pressure in the manometer chamber on the magnitude of the manometer deflexion—which varies according to the values of the initial pressures in the manometer chamber (the initial pressures in the manometer and heating-chambers must, of course, always be kept alike to avoid strains on the manometer and to keep it in its neutral zero-position); and (*b*) the work performed on the membrane-manometer itself and on the gas in the manometer chamber, which becomes slightly compressed during each manometer deflexion. For an unfavourably designed apparatus (*b*) can become very great. In the final experiments carried out here (*b*) was negligibly small (less than $\frac{1}{2}$ per mille of the measured quantity, apparatus No. 3). The effect of (*a*), however, had to be eliminated whenever measurements were made at various initial pressures P_0 (at times amounting to 5 per cent., apparatus No. 3).

The C_v-T-Curves obtained (fig. 3) show that the molecular heats of CH_4 and NH_3 sink with falling temperature below the values corresponding to rigid molecules (decrease in the energy of rotation of the molecule). With the exception of H_2 (observed by Eucken), these are the only gases for which

* It can also be shown theoretically that this should be expected.

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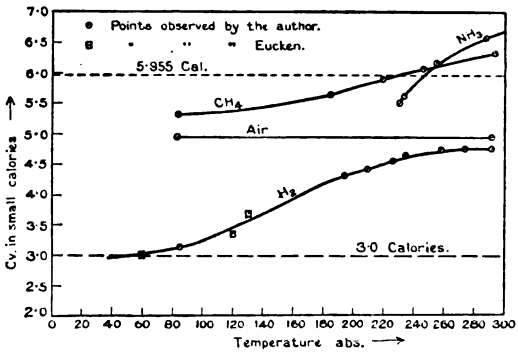
this property has yet been directly observed *. For CH_4 the value of C_v sank to a value of 5·30 cal./mol. T at a temperature $T=83^\circ$ abs.; for NH_3, to a value of 5·55 cal. at $T=229^\circ$ abs.

A few of the numerical results heretofore obtained by this method as a first contribution to the establishment of the C_v-T-Curves are shown in the table below (the author hopes soon to be able to complete the curves).

Fig. 3.



General view of the C_v-T-Curves for H_2, NH_3, CH_4 and air (see table).

The observations made on H_2, which were made primarily as a practical test of the applicability of the method at low temperatures, are in excellent agreement with those made by Eucken. The C_v values obtained in the neighbourhood of 200° abs. are also in harmony with the observations of Scheel at 197° abs.

The remarkably rapid fall of the C_v-T-Curve for NH_3 is noteworthy †.

* Since the observations described in this paper were made (discontinued January 1922), a paper by R. W. Millar (Journ. Amer. Chem. Soc. xlv. S. 874–881 (1923), No. 4) has appeared, which—by means of the steady flow method, measurements of C_p—qualitatively corroborates the observations made here on the decrease of C_v for CH_4 below the values corresponding to a rigid molecule having three degrees of freedom of rotation. Millar's measurements extended only down to a temperature of 142° abs.

† A number of theoretical considerations, which arose out of the results of the measurements of C_v for NH_3 and CH_4, led to the conclusion that at small pressures an observable and rapid fall of C_v with decreasing temperature would probably be observable also for a few other gases not yet investigated, such as PH_3 and AsH_3. These gases are presumably of the same molecular structure as NH_3; and according to the latest measurements of Rankine and Smith on the viscosities of these gases should have molecules with small diameters.

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TABLE.

Gas.	T.	P.	C_v cal./mol . T.	Remarks.
NH_3.	288	1/10 Atm.	6·65	Nernst : 6·61. Partington : 6·7.
	253	,,	6·25	
	243	,,	6·05	
	231	,,	5·60	
	229	,,	5·55	
	193	20 mm. Hg.	16·5	Polymerization or Condensation, abnormal C_v value.
CH_4.	278	1 Atm.	6·41	
	222	3/4 ,,	5·89	
	180	2/3 ,,	$5·68_5$	
	83	60 mm. Hg.	5·50[1]	
	83	250 ,,	18·00	Polymerization or Condensation.
H_2.	291	760 mm. Hg.	4·847	
	273	715 ,,	4·80	Eucken : 4·84.
	258	680 ,,	4·76	
	234	614 ,,	4·68	
	227	595 ,,	4·65	
	224	590 ,,	4·57	
	211	550 ,,	4·52	
	208	545 ,,	4·48	
	83	220 ,,	3·196	Eucken : 3·19.
C_2H_4.	286	1 Atm.	8·14	Scheel and Heuse : 8·19.
CO_2.	291	1 Atm.	6·81	,, ,, 6·86.
	291	½ ,,	$6·81_2$	
Air.	291	1 Atm.	4·979	Standard value taken from Scheel and Heuse.
	273	1 ,,	4·979	
	243	1 ,,	4·979	
	233	1 ,,	4·96	
	83	1/3 ,,	4·95	

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Miscellaneous Remarks.

The following remarks deal chiefly with some of the difficulties encountered in manipulating the apparatus. A few suggestions are also appended, indicating the general lines along which these difficulties may be eliminated and the method further developed and perfected for future measurements.

(*a*) Difficulties: the chief difficulty met with in completing a series of measurements was that of keeping in order the delicately suspended deflecting-mirror, which served as a member of the optically magnifying system necessary to accurately and expeditiously indicate the minute displacements of the membrane-manometer (the details, figures, etc., of the mirror-suspension will be given later in a longer paper); the fragile nature of the magnifying system (enabling accurate and rapid measurements of pressure-increments of the order of magnitude of $7 \cdot 10^{-4}$ g./cm.^{2}) made frequent breakdowns unavoidable—derangements often occurring near the end of a series of measurements, necessitating the discarding of all the readings thereby obtained. Another difficulty met with was that of keeping the manometer in its true zero-position and free from disturbing vibrations during a comparison-measurement. These disturbances were of two types:—first, rapid oscillations due to vibrations in the building (tramway-cars, etc.); and, second, gradual displacements of the manometer, to and fro, due to slight temperature discrepancies between the heating-chamber and the manometer chamber.

(*b*) Improvements: the lines along which the method may be experimentally improved are, to a great degree, already implicitly indicated in the above-mentioned difficulties. This demands the developing of an equally sensitive but at the same time less easily derangeable means of measuring the pressure-increments following the inductive impulses in the heating-chamber. The positive direction, therefore, in which the method is to be perfected is (as will be shown in the general theory of the method, which will be treated of in the paper mentioned above) in making accurate and rapid measurements of pressure-increments of a still smaller order of magnitude possible than were obtainable by the apparatus described in this paper.

The experimental part of this investigation was carried out in the Physico-Chemical Laboratories of the University of Berlin, and was finished in January 1922.

Sterling, Colorado, U.S.A.

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XIII. *Electric and Magnetic Spectroscopy.*

By Professor W. ARKADIEW, *Moscow* *.

THE velocity of very long waves in dielectrics depends on the dielectric coefficient ϵ_∞, which can be defined by electrostatic measurements taking in consideration the increase of the capacity of a condenser, and on the magnetic permeability μ_∞, which can be measured by a magnetometer. If the electromagnetic wave is very short, its electric and magnetic fields alternate so rapidly that the electric and magnetic particles fail to undergo any displacement and no electric or magnetic polarization can arise in a body of any influence on the velocity of the wave; there is no friction that produces a considerable absorption of waves of medium length. Therefore, the absorption of short waves is very small, and their velocity in matter does not differ from the velocity in vacuum; such are the X-rays, which hardly suffer any absorption; all bodies are transparent to X-rays, their velocity in matter is the same as the velocity in vacuum: the refractive index n of X-rays is equal to 1. This is because in the high-frequency electric fields of the X-ray waves the electrons and ions have not sufficient time for any perceptible displacement †. The vibrations of X-rays are outside the domain of electric qualities of matter in the region where the dielectric coefficient is equal to 1.

In the central part of the spectrum, where the frequency of the electromagnetic waves is equal or nearly so to the natural frequency of the electric centres, we have the region of vast variations of the refractive index n and of the dielectric coefficient ϵ, the *region of electric dispersion* and of strong absorption of rays, and the *region of electric absorption*. Here dielectric bodies obtain the so-called *electric conductivity of polarization* designated by σ.

The values of ϵ and σ, in the case of oscillating centres of a uniform group, are defined by the equations:

$$\epsilon = 1 + (\epsilon_\infty - 1)\frac{1-\nu^2}{\theta^2\nu^2 + (1-\nu^2)^2} \text{ and } \sigma = \frac{\epsilon_\infty - 1}{2T_0}\frac{\theta\nu^2}{\theta^2\nu^2 + (1-\nu^2)^2}, \quad . \quad . \quad . \quad (1)$$

where T_0 is the natural period of the centre, ν the relative frequency, equal to T_0/T; T is the period of the wave, and θ the coefficient of friction. (The vibrations become aperiodic when $\theta = 2$.)

* Communicated by the Author.

† A. H. Compton, Phil. Mag. xlv. p. 1121 (1923).

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The refractive index n and the coefficient of absorption k are determined by the following known expressions :

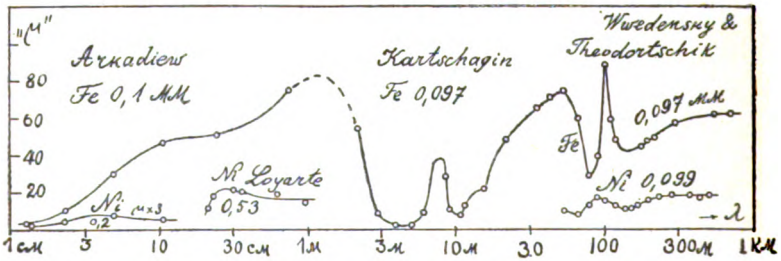
$$2n^2 = \sqrt{\epsilon^2 + \sigma'^2} + \epsilon \quad \text{and} \quad 2k^2 = \sqrt{\epsilon^2 + \sigma'^2} - \epsilon, \quad (2)$$

where $\sigma' = 2\sigma T$.

The magnetic properties of bodies are distinctly expressed in constant and slowly changing fields, where the magnetic permeability amounts to hundreds and thousands of units. On the other hand, in the waves of light and in the long infra-red waves, the magnetic properties of all bodies are equal and their magnetic permeability μ is equal to that of vacuum, *i. e.* $= 1$.

Therefore, the thermal waves have the same relation to magnetic centres as the X-rays to electric centres. This shows, that somewhere in the intermediate region, between the thermal oscillations and the slow electric vibrations, must be the *disappearance of the magnetic behaviour*, accompanied by *magnetic absorption* of the passing rays and by strong alterations of the magnetic permeability. This critical region

Fig. 1.



The magnetic spectra of iron and nickel wire for electromagnetic vibrations between 1 cm. and 1 km. wave-length.

occupies a very considerable part of the spectrum, at least from the length of waves of 1 cm. up to 1 km., as was shown by the investigations of Arkadiew *, Kartschagin †, Wwedensky and Theodortschik ‡, Gans and Loyarte §, and Nikitin ‖.

All along this line we find strong variations of the magnetic permeability (fig. 1) in weak fields.

* *Phys. Zeitschr.* xiv. p. 561 (1913) ; xxii. p. 511 (1921).
† *Ann. d. Physik*, lxvii. p. 325 (1922).
‡ *Ann. d. Physik*, lxviii. p. 429 (1921). *Physik. Zeitschr.* xxiv. p. 216 (1923).
§ *Ann. d. Physik*, lxiv. p. 209 (1921) ; lxvi. p. 429 (1921).
‖ *Zeitschr. f. Physik*, xxix. p. 288 (1924).

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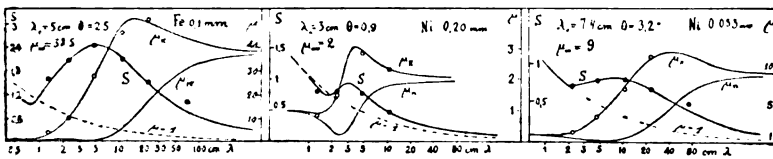
In the case of the very shortest waves this critical region was investigated in 1913, when there was found a big drop of the permeability in short Hertz waves: at $\lambda = 72{\cdot}7$ cm., $\mu \geqq 100$; at $\lambda = 10{\cdot}63$ cm., $\mu \geqq 30$; and at $\lambda = 1{\cdot}14$, $\mu = 3{\cdot}7$.

In this region iron and nickel show a strong absorption of electromagnetic waves, as can be seen in fig. 2, where the black dots show the values of S found in the experiments that are proportional to the coefficient of absorption k' of various waves in iron and nickel. They are represented as ordinates and the wave-lengths in vacuum as abscissæ.

Fig. 2.



The bands of magnetic absorption in iron and nickel wires and their apparent permeability μ_k and μ_n.

The material and the diameter of the wires are denoted on the diagram. In the same diagram are shown the proper wave-lengths λ_0 of the elementary magnets lying in this region, and the friction θ.

Within this region of absorption the magnetic permeability is subject to variation. In one case it even comes down to the value of 0·80.

Assuming that the elementary magnets in ferromagnetic metals under the influence of weak fields rotate under the same laws of viscous-elastic motion as are generally adopted for displacement of electric centres in dielectric bodies, we get for the permeability μ and *magnetic conductivity* ρ the following formula:

$$\mu = 1 + (\mu_\infty - 1)\frac{1-\nu^2}{\theta^2\nu^2 + (1-\nu^2)^2} \text{ and } \rho = \frac{\mu_\infty - 1}{2T_0}\frac{\theta\nu^2}{\theta^2\nu^2 + (1-\nu^2)^2}. \quad . \quad . \quad . \quad . \quad (3)$$

Four coefficients of the matter, ϵ, σ, μ, and ρ lead to the following form of the Maxwell equation:

$$\frac{\epsilon}{c}\frac{\partial E}{\partial t} + \frac{4\pi\sigma}{c}E = \text{curl } H$$

$$-\frac{\mu}{c}\frac{\partial H}{\partial t} - \frac{4\pi\rho}{c}H = \text{curl } E.$$

These equations give the values of the coefficient of refraction

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and of absorption * defined by the following expressions:

$$\left.\begin{aligned} 2n^2 &= \sigma'(\sqrt{\mu^2+\rho'^2}-\rho') = \sigma'\mu_n, \\ 2k^2 &= \sigma'(\sqrt{\mu^2+\rho'^2}+\rho') = \sigma'\mu_k, \end{aligned}\right\} \quad . \quad . \quad . \quad (4)$$

where $\rho' = 2\rho T$.

The coefficient of absorption k', which defines the decrease of the amplitude of the wave along the distance x according to the formula $e^{-k'x}$, is $2\pi k/\lambda = 2\pi\sqrt{\frac{\sigma}{c}}\cdot\sqrt{\frac{\mu_k}{\lambda}}$. The coefficient S, shown in the figure, is $\sqrt{\frac{\mu_k}{\lambda}}$. The lines show the theoretical course of the values μ_k and μ_n. The blank circles represent the values μ_k, calculated from the absorption of the waves in ferromagnetic wires †. The coincidence of the theoretical values with those derived from the experiments is fully satisfactory.

On the basis of the already existing experimental materials such determinations could be performed with wires of different diameters. Knowing the intensity of magnetization up to saturation I_∞ and the density of matter δ, it is possible, supposing that the oscillating elementary magnets are only of one type, to calculate their radius a according to the following formula:

$$a = I_\infty T_0 \sqrt{\frac{5}{3\pi\delta(\mu_\infty - 1)}} \text{ cm.}$$

These values for wires of different diameters together with other quantities are given in the following table:—

	Nickel.			Iron.					
	Arkadiew.		Gans.	Arkadiew.					
2R mm....	0·053	0·20	0·54	0·05	0·10	0·20	0·30	0·40	0·50
λ_0 cm. ...	7·4	3·0	24·3	5·9	5·0	3·55	3·0	2·5	2·3
μ_∞	9·0	2·0	12·0	35·0	38·5	27·5	22·2	18·7	14·5
θ.....	3·2	0·90	1·3	2·0	2·5	2·0	1·7	1·7	1·6
$10^{-10}.\rho_{max.}$	0·50	0·55	0·5224	4·3	4·5	5·7	6·3	6·3	5·5
$10^8.\ a$ cm.	1·12	1·28	3·11	1·49	1·20	1·01	0·96	0·87	0·92

* The general expressions for n and κ are $2n^2 = \sqrt{(\epsilon^2+\sigma'^2)(\mu^2+\rho'^2)} + \epsilon\mu - \sigma'\rho'$ and $2\kappa^2 = \sqrt{(\epsilon^2+\sigma'^2)(\mu^2+\rho'^2)} - \epsilon\mu + \sigma'\rho'$; from these equations we get (2) and (4) as special cases. W. Arkadiew, *Physik. Zeitschr.* xiv. p. 928 (1913); *Ann. d. Physik*, lxv. p. 643 (1921).

† W. Arkadiew, *Ann. d. Physik*, lviii. p. 105 (1919).

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We see that, notwithstanding the great inconstancy of the values λ_0, μ_∞, and θ, the values $\rho_{max.}$ i. e. ρ near $\nu=1$ and a show a certain stability.

The instability of the magnetic spectra and their dependence on the properties of the material for the wire, especially on its diameter (fig. 1), is connected with the known unsteadiness of the ferromagnetic qualities in general. Their natural period T_0 depends upon the directing internal field which keeps the elementary magnets in their natural state of equilibrium, and defines the value of permeability μ_∞ in weak fields. It would better answer the purpose to analyse the magnetic spectra of iron magnetized by strong constant external field.

From the above-mentioned formulæ (2) and (4) we see that n and k in the case of electric and magnetic dispersion are defined by the binoms :

$$r+\alpha, \qquad r-\alpha,$$
$$\mu_k=r+\beta', \qquad \mu_n=r-\beta',$$

where α replaces ϵ and μ, β' replaces σ' and ρ', and $r=\sqrt{\alpha^2+\beta'^2}$.

The researches on the course of the values $r\pm\alpha$ are the object of the theory of electric dispersion and absorption and, as a special case, the ordinary optic dispersion ; the study of the course of the values $r\pm\beta'$ forms the object of the theory of magnetic dispersion and absorption.

Lately the binoms μ_k and μ_n have been the subject of electrotechnical researches, where by means of them the theoretic analysis of electromagnetic processes has been accomplished, by which it has been shown that the absorption of energy in iron is due not only to the damping friction θ of the rotating elementary magnets, but also to other causes, as hysteresis and eddy currents (Uller *, Truxa †, Tonks ‡, Gans §).

The researches on the quantities $\mu=\sqrt{\mu_k\,.\,\mu_n}$, $2\rho'=\mu_k-\mu_n$, ρ, μ , and μ_n in their dependence on the wave-lengths λ, for various ferromagnetic metals and their combinations, *i. e.* their *passive magnetic spectra*, form the object of *passive magnetic spectroscopy* ‖. The difference between this and

* *Verh. d. Deutsch. Phys. Ges.* iv. p. 31 (1923).

† *Archiv für Electrot.* xii. p. 354 (1923).

‡ Phys. Rev. xxiii. p. 221 (1924).

§ *Phys. Zeitschr.* xxiv. p. 232 (1923).

‖ This subject is treated in the monograph "Magnetic Spectroscopy" by W. Arkadiew: No. 4 of Transactions of the State Electrical Research Institute, Moscow, 1924 (in Russian, with the abstract in English). Also No. 6 of Transactions "Researches in Electromagnetism," edited by Arkadiew, and *Zeitschrift f. Physik*, xxvii. p. 37 (1924) ; xxviii. p. 11 (1924).

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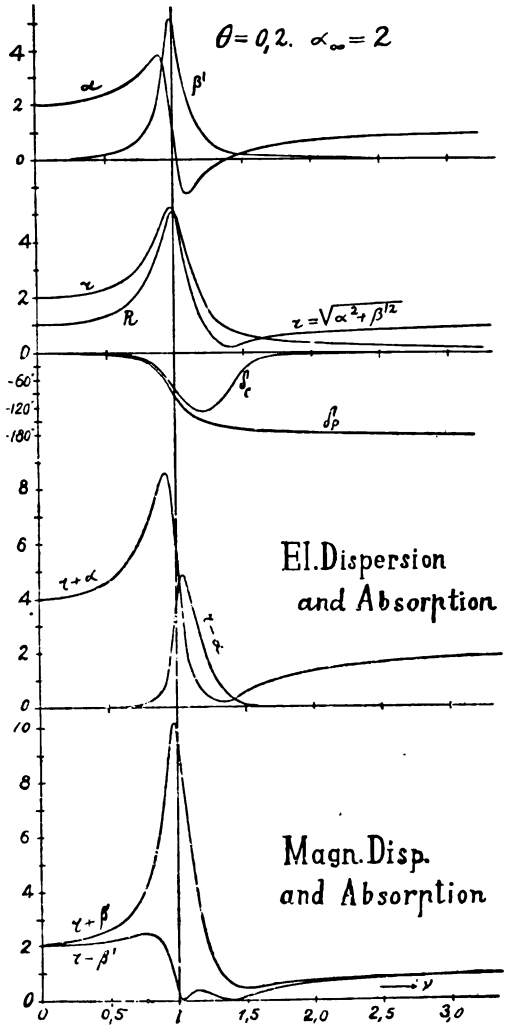
Fig. 3.



R = resonance of electric and magnetic centres.

δ_p = the retardation of their phase and the phase of the polarization against the phase of the field.

δ_c = the retardation of the phase of induction.

r = the value $\sqrt{a^2+\beta'^2}$; the coefficient of refraction n in dielectric bodies is determined by $2n^2 = r + a$; the coefficient of absorption k in them by $2k^2 = r - a$; the coefficient of apparent permeability $\mu_k = r + \beta'$ and $\mu_n = r - \beta'$.

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the old *passive electric spectroscopy* is that the former investigates the influence on matter of the *electric vector* of the electromagnetic wave, and the latter, of the *magnetic vector* of the same wave. We find that both these branches of the general electromagnetic spectroscopy have equal rights.

Magnetic spectroscopy forms the special object of study in the Moscow Magnetic Laboratory.

I. University and State Electrical
Research Institute,
Moscow, 7 June, 1924.

XIV. *A Physical Interpretation of Bohr's Stationary States.* By G. P. Thomson, *M.A., Professor of Natural Philosophy in the University of Aberdeen and Fellow of Corpus Christi College, Cambridge* *.

Monsieur L. de Broglie has shown in a paper in this Magazine † that the stationary states of an electron can be regarded as determined by the condition that the orbital motion of an electron can only be stable if the length of the path is such as to be in tune with the "phase wave" which M. de Broglie supposes to accompany the electron.

A similar result, in the case of the hydrogen atom, can be obtained, without the necessity of postulating waves with a velocity greater than that of light, by the development of the model proposed by Sir J. J. Thomson ‡ to explain the existence of bundles of energy in radiation.

Suppose the electron to be attached to the nucleus by a tube of force which is to be regarded, not as on the classical theory as spreading out to fill all space, but as forming a connexion of limited, though possibly varying cross-section between the two charges. Suppose, as on the classical theory, that the tension of the tube provides the attraction between the electron and the nucleus, and that the tube possesses energy and therefore mass. It will thus be able to transmit waves, and the condition that will be taken as determining the possible states is that the vibrations in this tube shall be in tune with the period of the orbit. Only when this is the case can the motion be strictly periodic, for there will always be in practice some slight external effects to produce disturbances.

* Communicated by the Author.
† Phil. Mag. xlvii. p. 446.
‡ Phil. Mag. xlvii. p. 737.

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The condition required is that

$$\int^{T} V\,dt/\lambda = n, \text{ an integer,}$$

where the integral is taken over a complete period of the orbit, V is the velocity of the waves and λ is the wave-length. Making the supposition that the waves with which we have to deal are the transverse vibrations of a stretched string, λ is $2r/m$, where m is an integer and r the length of the tube, so the condition will be satisfied for *all* modes of vibration if

$$\int^{T} V\,dt/2r = n.$$

For an elliptic orbit of eccentricity ϵ, semi-latus rectum l and for which $r^2\dot{\theta} = p$, the condition becomes

$$n = \int_0^{\pi} Vl\,d\theta/p(1+\epsilon\cos\theta),$$

and if V is taken as a constant a simple integration gives

$$n = V\pi l/p\,\sqrt{1-\epsilon^2}.$$

Substituting for p, l, ϵ in terms of the axes this becomes

$$n = V\pi\,\sqrt{am/e} \quad \text{or} \quad a = n^2e^2/V^2\pi^2m,$$

where a is the semi-major axis, m the mass of the electron, and $\pm e$ the charges on nucleus and electron. This reduces to Bohr's condition

$$a = n^2h^2/4\pi^2e^2m$$

$$\text{if} \qquad V = 2e^2/h.$$

The value of V thus found is not equal to the velocity of light, with which waves would travel on a free tube of force on the classical theory. The proposal is to account for the failure of the classical theory by ascribing different properties to the tube of force according as to whether it is fixed only at one end and radiates into space, or forms a bond between an electron and a nucleus. If in the latter case the velocity of waves along it is taken to be $2e\mathrm{E}/h$ where E is the charge on the nucleus, a simple extension of the above accounts also for the stationary states of ionized helium, and gives approximately the energy of the K ring of electrons. On this view the non-dimensional quantity $hc/e\mathrm{E}$ is a measure of the extent to which such a "bound" tube of force departs from the condition of the free tube.

Aberdeen,
March 14.

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XV. *The Spectrum of Sodium at Low Voltages.* By F. H. NEWMAN, *D.Sc., A.R.C.S., Professor of Physics in the University College of the South-West of England, Exeter* *.

[Plate IV.]

1. INTRODUCTION.

ALTHOUGH the theory of the atom, as developed by Bohr, Sommerfeld, Rubinowicz, etc., has not reached that state which gives a complete representation of spectra other than those of hydrogen and helium, yet it yields a general indication of the structure. Considering the case of the sodium atom, the 1σ ring represents the outermost stable orbit and the innermost unstable orbit of the normal atom, and all the principal series doublets, $1\sigma - m\pi$, are emitted when the valency electrons in various atoms fall from one of the π rings to the 1σ orbit, the series converging at 1σ. The first subordinate series lines are produced by electrons falling from the $m\delta$ rings to the 1π ring, and the second subordinate series when the electrons are transferred from the $m\sigma$ to the 1π rings. Interorbital motions, other than those mentioned, give rise to the fundamental series and various combination lines, although in such interorbital motions the selection principle allows only those transitions in which the azimuthal quantum number changes by unity. The azimuthal quantum numbers of the $m\sigma$, $m\pi$, $m\delta$, and $m\phi$ orbits are, respectively, 1, 2, 3, and 4, so that interorbital transitions from the $m\pi$ to the $m\sigma$ or the $m\delta$ levels are possible, but transitions from the $m\sigma$ to the $m\delta$ orbits are precluded. It is true that in some cases lines are observed which represent interorbital movements where the change in azimuthal quantum number is according to Sommerfeld 2 units, such, for example, as the pair λ 4642·2, 4641·6 in the potassium spectrum, but the excitation of this pair is explained by the incipient Stark effect. This doublet, and the corresponding one in the sodium spectrum, are excited also in low-voltage arcs when the electron density is great. In this case the excitation is caused, apparently, by the interaction of atomic fields of neighbouring positive ions and electrons. Such atomic fields are probably many times greater than the intensity of the applied external electric force.

The electron is displaced from the 1σ ring to the next

* Communicated by the Author.

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outer orbit—the 1π ring—whenever the sodium atom receives energy, either by bombardment or by the absorption of radiation, equivalent to 2·1 volts, and the valency electron being now in a temporary orbit falls to the 1σ ring and, in so doing, gives up the quantum of energy received during its ejection from the 1σ ring as a quantum of radiation $h\nu$ with the emission of the D lines. When energy equal to, or greater than, 5·12 volts is communicated to the atom the valency electron is displaced from its normal orbit and leaves the atom and, in returning, may occupy temporarily any one of the stationary orbits, the dimensions of which are large compared with the X-ray orbits, before it reaches the 1σ ring. The many electrons returning in the different atoms will do so by various different steps and the many-line spectrum results, the intensities of the different lines representing to some approximation the chances of the corresponding interorbital transitions.

The atom also absorbs radiation of frequency corresponding to a $1\sigma - m\pi$ change and accordingly the electron is displaced to any of the $m\pi$ rings. Rayleigh * has observed that the sodium line λ 3303, incident on sodium vapour, excites the D lines and λ 3303, so that electrons within the 2π orbit may fall directly to the 1σ orbit, or they may pass, directly or indirectly, to the 1π orbit and thence to the normal orbit 1σ. Absorption and fluorescence phenomena indicate that the electron can be displaced directly from its normal orbit to any of the π rings but not to others. It is to be expected, therefore, that similar displacements would be produced by electronic bombardment. Until recently experimental confirmation of this latter expectation was not available, although Franck and Einsporn †, who used a "photo-electric" method, had shown that the photo-electric current in mercury vapour increased suddenly as the critical energy for each of the known orbits was attained. In spite of this electron displacement to these orbits spectroscopy gave no evidence of the successive emission, line by line, all the results obtained indicating the existence of a single line spectrum at resonance potential, and an abrupt transition to the entire arc spectrum as the energy of the bombarding electrons increased to the ionization potential.

Following a suggestion made by Birge, and utilized by Foote and Meggers ‡, a graphical representation of the

* See Strutt, Proc. Roy. Soc. A, vol. xcvi. p. 272 (1919).
† *Zeits. f. Phys.* 2. i. p. 18 (1920).
‡ Phil. Mag. xl. p. 80 (1920).

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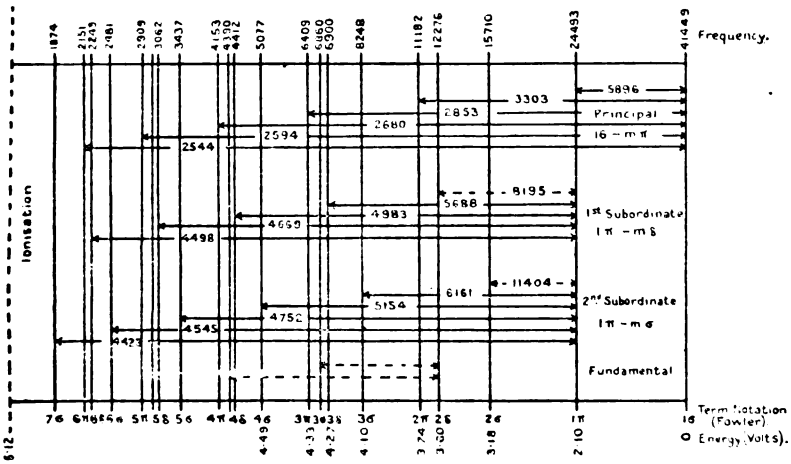
energy levels in the sodium atom is shown in fig. 1. Regarding the lines as representing the non-radiating orbits, the nucleus is supposed situated away to the right of the diagram, and the actual sodium lines correspond to the transition of electrons from orbits on the left to orbits on the right. The π orbits are really double but their separation is too small to be represented, and in the diagram only that orbit corresponding to the higher energy level has been shown. The lines really represent portions of the elliptical or ring orbits about the nucleus, 1σ being the outermost stable orbit of the valency electron. The first doublet of the principal

Fig. 1.



Graphical representation of sodium atom.

series is produced by the electron falling from the 1π to the 1σ orbit, the line of longer wave-length—λ 5896—having a frequency equal to the difference of the frequencies characterizing these orbits, viz. 41449–24493. The second doublet of the principal series is emitted when the electron falls from the 2π orbit to the 1σ orbit, etc. The first line of the first subordinate series is represented by an electron falling from the 2δ ring to the 1π ring, and the other lines of this series correspond to ejections from the $m\delta$ orbits to the 1π orbit. The falls from the $m\sigma$ orbits to the ring represented by 1π yield the second subordinate lines; falls from the ϕ orbits to the 2δ orbit give the fundamental series lines, and the various combination lines can be considered in the same way. All horizontal lines extending

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between the orbits indicate emission lines produced by energy falls between these orbits. The dotted lines represent emission lines in the infra-red.

The energy level of any particular orbit can also be expressed in terms of the potential difference through which an electron must fall in order to accumulate kinetic energy equivalent to the quantum of radiation corresponding to this energy. The potential difference V is given by the quantum relation $Ve = h\nu$, where e is the unit of charge, h is Planck's constant, and ν the frequency. For example, in order to displace the valency electron from the 1σ orbit to the 1π orbit the energy of the bombarding electron must be equal to that which it would possess by falling through 2·1 volts—the resonance potential of sodium vapour,—and the displaced electron, being then in a temporary orbit, falls back to the 1σ orbit giving up the quantum of energy eV, received at the collision, as a quantum of radiation energy $h\nu$ of frequency ν. In a similar manner, bombardment with electrons of energy corresponding to 3·74 volts should eject the valency electron to the 2π orbit. Theoretically, an electron of this energy should be capable of ejecting the valency electron to the 1σ, 2σ, or 2δ orbit, for such ejectments require energy less than 3·74 volts. If sodium atoms are bombarded with electrons possessing this energy, the lines λ 5896, 5890; λ 8195, 8183; λ 11404, 11382; and λ 3303, 3302 should be emitted by interorbital transfers permitted by the quantum theory. In a similar manner, by increasing the energy of the bombarding electrons to values below the ionization potential the other lines in the various series should be excited, until when the energy has reached 5·12 volts the entire arc spectrum of sodium should appear.

Recently Eldridge *, using a three-electrode discharge tube in which electrons emitted from an incandescent cathode were accelerated by a potential between the grid and cathode and entered a force-free space between the grid and plate, has obtained such a line-by-line emission with mercury vapour as the impacting energy increased to those values sufficient to eject the electrons to their proper orbits, and he has stated that the previous failure to observe this step-by-step emission is explained by the space charge effect lowering the impacting energy except at the immediate surface of the anode. Formerly, spectroscopic investigation of mercury vapour bombarded with electrons of energy less than the ionization potential—10·4 volts—had shown the

* Phys. Rev. xxiii. p. 685 (1924).

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lines $1S-1p_2$ and $1S-1P$ only, but Eldridge has photographed the line $1S-1p_2$ at 7 volts, 4 additional lines due to electrons returning from the 2S or $1s$ levels at 8·4 volts, 8 additional lines at 8·9 volts, and 16 more lines at 9·9 volts, in full agreement with the theory and with the photoelectric experiments of Franck and Einsporn.

Hughes and Hagenow *, employing a large equipotential source of electrons by fitting a nickel cylinder over an alundum tube, heated internally by a tungsten spiral, showed definitely that lines in the principal series of cæsium appear in the order, and within 0·1 volt, of the potential required by the theory. They found the first and second subordinate series lines more difficult to observe, but these lines did appear below the ionization potential of cæsium vapour, viz. 3·9 volts.

From a study of fig. 1 it is evident why only the principal lines show absorption. The valency electron, lying normally in the 1σ orbit, can be displaced directly to one of the $m\pi$ orbits, the necessary energy for such a displacement being provided by the energy quanta abstracted from the incident light and resulting in light absorption of corresponding frequency.

Foote, Meggers, and Mohler †, who studied the excitation of the sodium spectrum, employed a grid mounted extremely close to a tungsten hot-wire cathode and in metallic contact with a concentric hollow cylinder of relatively large diameter. By regulating the temperature a vapour pressure was obtained for which relatively few electronic-atomic collisions occurred over the short accelerating field between the grid and cathode. The majority of the electrons passed into the force-free space between the grid and the plate and had, at the instant of collision, a velocity corresponding to the impressed field. These experimenters found that only the single line spectrum, consisting of the D lines, was excited above the resonance potential and below the ionization potential. With potential differences above the latter the entire arc spectrum appeared. An interesting feature was the excitation of λ 3427 which has the notation $\nu = 1\sigma - 2\delta$. This line represents an interorbital transfer where the change in the azimuthal quantum number is 2 units, and apparently contradicts the Bohr principle of selection as applied by Sommerfeld to spectra of non-hydrogenic type, but, as explained previously, the appearance of the line is

* Phys. Rev. xxiv. p. 229 (1924).
† Astrophys. Jour. lv. p. 145 (1922).

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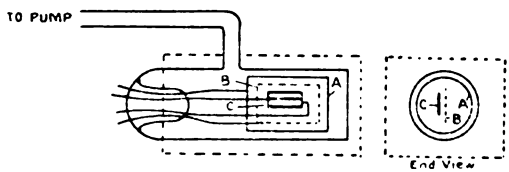
accounted for, probably, by the electric forces between neighbouring electrons and positive ions.

It was decided to repeat the work of these investigators with sodium vapour, minimizing the space charge effect within the discharge tube. It should then be possible to bring out the lines, step-by-step, in accordance with the theory. The apparatus employed is shown diagrammatically in fig. 2.

Fig. 2.



2. Experiments.

The discharge tube—about 1 cm. in diameter—was of quartz and had a quartz plate cemented at one end. The source of the electrons was a tungsten filament cathode C consisting of three tungsten wires arranged in parallel, each wire being 1·2 cm. long. By using three tungsten wires in this way a good supply of electrons was obtained without raising the filament to very bright incandescence. The nickel gauze grid B, placed not more than about 1·5 mm. away from the cathode, was in electrical contact with the nickel cylinder A which completely surrounded the cathode and made the interior of the tube a constant potential region. The electrons, accelerated by a potential difference applied between the negative end of the cathode and the grid, entered the constant potential space between A and B. The whole tube, which contained a small quantity of sodium metal, was enclosed within an electric furnace the interior of which was maintained at 350° C. At this temperature the vapour pressure of sodium, although not known with any great degree of accuracy, is certainly below 0·1 mm. of mercury *. The electron currents used were about 2 milliamperes.

In consequence of the space charge effects it was necessary to focus on the slit of the quartz spectrograph light coming from the immediate neighbourhood of the grid, and throughout the period that spectroscopic observations were

* See Hackspill, *Comptes Rendus*, cliv. p. 877 (1912).

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being made the discharge tube was connected to a Cenco-Hyvac oil pump which, running continuously, insured that the residual gas pressure was maintained well below 0·01 mm. of mercury. If the tube was not continuously exhausted in this manner, the gas pressure rose to such a value that no luminosity appeared between the grid and the plate even with accelerating voltages exceeding the ionization potential of sodium vapour. The spectrograms at different accelerating voltages were photographed on special rapid panchromatic plates.

The potential difference, as measured between the cathode and grid, does not give necessarily the energy of the electrons at the instant that they pass through the grid. There are other factors which influence their kinetic energy such as contact potential, fall of potential along the lead-in wires and along the filament, and the initial velocity of the electrons emitted from the cathode. At dull red heat about 3 per cent. of these electrons have an initial velocity corresponding to 0·5 volt. The discrepancy between the apparent and true values of the electron energy can be determined and allowed for by measuring the ionization potential. The experimental value was 4·7 volts, and as the calculated value is 5·1 volts, the correction to be applied is 0·4 volt. This correction has been made in all the measurements quoted.

As the accelerating voltage was raised to 2·2 volts a yellow glow appeared in close proximity to the grid and plate. Increasing the voltage still further the colour of the radiation changed to greenish-yellow and extended a short distance from the electrodes, until at 5·2 volts the whole of the space between the grid and plate was filled with the glow. From the appearance of the tube it is evident that the space charge lowers the effective potential except in the immediate neighbourhod of the electrodes. The various spectrum lines which appeared at different voltages are given in Table I.

The spectrograms obtained with different excitation voltages are shown in Plate IV. In the first one the doublet λ 5896, λ 5890 appears at 2·2 volts. The energy of the electrons is sufficient to displace the valency electron to the 1π orbit. At 3·18 volts the doublet λ 11404, λ 11382 should be additional to the D lines, but it is far beyond the range of the plate. Similarly at 3·6 volts λ 8195, λ 8183 should appear, but this doublet also is outside the range of the plate, so that at 3·74 volts the only lines on the plate should be λ 5896, λ 5890, λ 3303, and λ 3302. The second spectrogram at 4·0 volts shows these lines and no others.

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TABLE I.

Series.	Wave-length.	Excitation voltage.	
		Experimental.	Calculated.
$1\sigma-1\pi$	λ 5890 λ 5896	2·2 volts.	2·10 volts.
$1\pi-2\sigma$	λ 11382 λ 11404	—	3·18
$1\pi-2\delta$	λ 8183 λ 8195	—	3·60
$1\sigma-2\pi$	λ 3302 λ 3303	4·0	3·74
$1\pi-3\sigma$	λ 6154 λ 6161	4·4	4·10
$1\pi-3\delta$	λ 5683 λ 5688	4·6	4·27
$1\sigma-3\pi$	λ 2853	—	4·33
Complete arc spectrum		..... 5·2	5·12

In a similar manner λ 6161, λ 6154 should be the next lines to appear, and spectrogram No. III. contains these additional lines at 4·4 volts. The doublet λ 5688, λ 5683 made its appearance at 4·6 volts (spectrogram No. IV.), but with the exposures employed no further lines were excited until the voltage reached 5·2 volts, when ionization set in (spectrogram No. V.). It is difficult to differentiate between the excitation of lines within the range 4·6–5·2 volts, for the number of collisions resulting in excitation is probably small at the actual critical voltage but increases as the latter is exceeded.

The results indicate that the valency electron within the sodium atom is displaced to different orbits by inelastic impacts with bombarding electrons possessing the requisite energy, and line-by-line excitation is possible. The line λ 3427 photographed by Foote, Meggers, and Mohler at the ionization potential was not observed in the present experiments, but the electron currents employed were very small compared with those used by the previous investigators, and it is only in the presence of strong electrostatic fields, either external or internal, that this line becomes prominent.

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3. Summary.

On the basis of Bohr's theory of atomic structure it is shown that the normal operation of an arc below ionization should result in the excitation of a line-by-line spectrum corresponding to changes of orbit involving less energy than the ionizing potential. Previous attempts to obtain such an emission with sodium vapour have failed. In the present work a three-electrode discharge tube was used, and the electrons emitted from a heated tungsten wire cathode were accelerated by a potential difference applied between the grid and cathode. Photographic observations showed the development of the spectrum in the order of the potential predicted by theory. At 2·2 volts λ 5896, 5890 only appear. At 4·0 volts the lines λ 3303, 3302 are excited, and the lines λ 6161, 6154 and λ 5688, 5683 are emitted at 4·4 and 4·6 volts respectively, in agreement with theory.

The cost of the quartz spectrograph, used in the experiments described above, has been defrayed by a Government grant, through the Royal Society, for which the author wishes to express his sincere thanks.

XVI. *Some Remarks on the Fulcher Hydrogen Bands.* *By* G. H. Dieke *.

SEVERAL papers have appeared recently which deal with the regularities in the secondary spectrum of hydrogen discovered by Fulcher † in 1912. Most of them give interpretations of these regularities which agree in principle with the one given first by Lenz ‡, but which differ in details from it and among themselves. M. Kiuti § connects the branches in the red and green part of the spectrum by a Q-branch discovered by him. Quite recently W. E. Curtis ‖, making use of an investigation of A. S. Allen ¶, gives a critical revision of the numeration of the band-lines, and offers an explanation of the connexion between the different branches.

In an earlier paper ** the author showed that there is

* Communicated by Prof. P. Ehrenfest.

† G. S. Fulcher, *Phys. Zs.* xiii. p. 1137 (1912); Astroph. Journ. xxxvii. p. 60 (1913).

‡ W. Lenz, *Verh. d. Phys. Ges.* xxi. p. 632 (1919).

§ M. Kiuti, Proc. Phys.-Math. Soc. Japan, (3) v. p. 9 (1923).

‖ W. E. Curtis, Proc. Roy. Soc. A, cvii. p. 570 (1925).

¶ A. S. Allen, Proc. Roy. Soc. A, cvi. p. 69 (1924).

** G. H. Dieke, Proc. Roy. Acad. Amsterdam, xxvii. p. 490 (1924).

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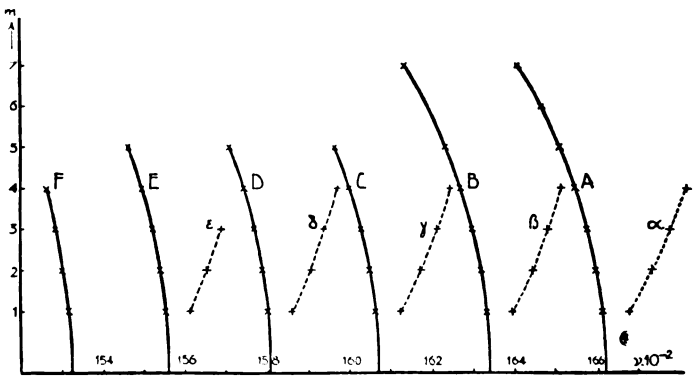
another possibility of explaining the regularities which gives quite different results regarding the structure of the molecule which emits the bands. Therefore it seems desirable to give a comparison between the two different possibilities.

For brevity's sake we shall call the interpretation of the bands accepted by Lenz, Kiuti, Allen, and Curtis "Interpretation A" (or simply "A") and the one proposed by the author "Interpretation B," and shall refer for "A" mainly to the paper of Curtis as being the most recent one and containing the most details.

1. The lines in one band (m variable, n_1 and n_2 constant)*, as well as the corresponding lines of the bands in one group (n_1 variable, $\Delta n = n_1 - n_2$, and m constant), follow Deslandres's law. Owing to the small moment of inertia of the hydrogen molecule, the spacing of the lines in one band will be of the same order of magnitude as the spacing of the bands in one group. Therefore, if a parabolic series is given, one cannot immediately see from the relations between the wave-numbers alone whether the variable is m or n.

Fig. 1.



In fig. 1 the regularities in the red are represented graphically. The lines on a horizontal, which are represented by the same sign ($\times$ or $+$), form a "Fulcher band" (called here, as in Curtis's paper, *horizontal series*), and the lines connected by the curves the extension of the Fulcher triplets (*vertical series*). For simplicity, in the beginning we shall leave out of consideration the lines connected by the dotted curves.

* m is the rotational, n the oscillation-quantum number.

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Now the two assumptions interpret the regularities in a different manner :—

"*A*" says the horizontal series form a band, whereas "*B*" considers the vertical series as branches of a band. The different vertical series are considered by "*B*" as different bands of a group ($n_1 - n_2 =$ constant). The same was done by Curtis with respect to the different horizontal series. The numerical relationships as expressed by Deslandres's law cannot help us to decide between the two assumptions, as they are consistent with both.

But the lines of a vertical series can be represented exactly by

$$\nu = \mathrm{A} - \mathrm{C}m'^2 - \mathrm{D}m'^4 \quad (m' = 1{\cdot}5\ ;\ 2{\cdot}5, \ldots.), \quad . \quad (1)$$

in which the term $\mathrm{D}m'^4$ is only a small correcting term. If we accept "*A*," the existence of the relation (1) must be attributed to chance or, as this is not very likely, to a property of the molecule which is still unknown and which is found in no other band-spectrum. This difficulty does not exist if we take assumption "*B*," for according to it the vertical series are interpreted as Q-branches, and (1) is the theoretical formula for them.

2. The *structure of one band* is not one familiar to us from other band-spectra. If we take interpretation "*A*," only a P- and P′-branch exist, for Kiuti's assumption that the bands in the green form R-branches leads to serious difficulties, and has therefore been abandoned also by Allen and Curtis. The existence of a P-branch without a Q- or R-branch belonging to it ought not to be considered as a serious difficulty; but the connexion between the P- and P′-branches is not the same here as in the helium bands, where it can be understood theoretically. If the interpretation "*B*" is accepted, thus far only a Q- and an R-branch could be identified. But it is very probable that several other lines belong to the same bands, and form perhaps a P-branch. There is, however, no sufficient criterion which would allow us to decide whether a certain arrangement is right or not. For the same reason the arrangement of the lines in the positive branches (the dotted ones in fig. 1) can be considered only as provisional. Only further experimental investigation can give sufficient certainty.

3. *Intensity of the Lines.*—We expect that in the hydrogen bands, owing to the small moment of inertia of the carrier, the first or second line will have the maximum

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intensity at ordinary temperatures, and that the intensities of the following lines will diminish very rapidly, so that each band only contains a few lines. However, we can predict nothing about the intensities of the different bands of one group.

In our case the distribution of intensities is a normal one in the horizontal series, whereas in the vertical series the even lines are much weaker than would be expected from the intensities of the neighbouring odd lines. It seems very difficult to give an explanation of these alternating intensities on the basis of assumption "*A*." If, however, we accept the interpretation "*B*," we are led to the conclusion that each vertical series consists in reality of two different series, a strong one and a weak one. Then the odd lines belong to the transitions $m-\frac{1}{4}\rightarrow m-\frac{1}{4}$, and the even lines to $m+\frac{1}{4}\rightarrow m+\frac{1}{4}$, and formula (1) must be written (if we neglect the correcting term Dm'^4)

$$\left.\begin{array}{ll} \nu=A-4C(m-\frac{1}{4})^2 & \text{odd lines} \\ & \qquad m=1,\,2,\,3 \\ \nu=A-4C(m+\frac{1}{4})^2 & \text{even lines} \end{array}\right\} \quad . \quad . \quad (2)$$

With the half-quantum interpretation (formula (1)) it could not be understood why the line corresponding to the transition $0{\cdot}5\rightarrow 0{\cdot}5$ is absent. With quarter effective quantum numbers no such line (which would here be due to the transition $0{\cdot}25\rightarrow 0{\cdot}25$) can exist because, according to a general rule of Bohr, *one* is the smallest possible value of m. A strong support for this conception is that recently exactly the same intensity anomalies have been found in the negative nitrogen bands *, and the author † was able to show that one does not come to any contradiction if one considers the weak lines as forming one branch and the strong lines as forming another one. It is further remarkable that quarter effective quantum numbers have been found to exist in almost all bands which must be attributed to pure elements.

4. *Variation of the Intensities with Temperature.*—Goos ‡ measured the intensities of the red Fulcher triplets accurately at three different temperatures, and McLennan and Shrum § observed the many-lined spectrum at the temperature

* M. Fassbender, *Zs. f. Phys.* xxx. p. 73 (1924); see also R. Mecke, xviii. *Phys. Zs.* xxv. p. 597 (1924).

† G. H. Dieke, *Zs. f. Phys.* xxxi. p. 326 (1925).

‡ F. Goos, *Zs. f. Phys.* xxxi. p. 229 (1925).

§ J. C. McLennan and G. M. Shrum, Trans. Roy. Soc. Canada, (3) p. 177 (1924).

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of liquid hydrogen. In the following tables the results of these authors are given. In Table I. the lines are arranged according to interpretation "*A*" and in Table II. according to "*B*." The first column gives the author's notation, the

TABLE I.

	λIÅ.	M.	W.	T=19°.	T=87°.		T=295°.		T=495°.	
					2·5.	29.	2·0.	17.	1·4.	$18\rho/\rho_0 10^4$.
A (1)	6018·29	10	9	++	100	100	100	100	100	100
B (1)	6121·76	10	10	++	128	109	108	100	113	100
C (1)	6224·81	9	10	++	125	114	101	94	105	92
D (1)	6327·07	8	8	++	88	85	71	57	72	57
E (1)	6428·10	5	2	++	24	32	23	31	23	26
A (3)	6031·80	10	5	=	100	100	100	100	100	100
B (3)	6135·34	8	6	=	135	144	105	105	106	94
C (3)	6238·39	8	6	=	74	67	77	60	90	66
D (3)	6340·57	6	2	—	—	33	40	29	51	37

TABLE II.

	λIÅ.	M.	W.	T=19°.	T=87°.		T=295°.		T=495°.	
					2·5.	29.	2·0.	17.	1·4.	$18\rho/\rho_0 10^4$.
A (1)	6018·29	10	9	++	100	100	100	100	100	100
A (2)	23·74	7	4		16	19	27	34	34	41
A (3)	31·80	10	5	=	23	36	43	62	73	106
B (1)	6121·76	10	10	++	100	100	100	100	100	100
B (2)	27·40	9	2		16	20	37	38	49	53
B (3)	35·34	8	6	=	24	48	42	65	68	100
C (1)	6224·81	9	10	++	100	100	100	100	100	100
C (2)	30·23	7	2		13	13	29	31	33	39
C (3)	38·39	8	8	=	14	31	33	39	63	76
D (1)	6227·07	8	8	++	100	100	100	100	100	100
D (2)	32·46	5	1		—	16	24	30	44	46
D (3)	40·57	6	2	—	—	14	24	32	51	68

second one the wave-lengths according to Merton and Barratt *, and the following two the intensities as observed by Merton and Barratt (M) and Watson (W)†. The fifth column

* T. R. Merton and S. Barratt, Phil. Trans. A, ccxxii. p. 369 (1922).
† H. E. Watson, Proc. Roy. Soc. A, lxxxii. p. 189 (1909).

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contains the observations of McLennan and Shrum, and the following ones the measurements of Goos at the given temperatures and densities (ρ). + + means that the line is strongly enhanced at $T=19°$, — resp., and = that it is weakened, resp. strongly weakened. Goos's measurements are multiplied by such a factor that the first line in every band has the intensity 100.

With increasing temperatures the lines which belong to higher m must be enhanced, and they must be weakened at low temperatures. This behaviour of band-lines with variations of temperature has been confirmed experimentally in all cases where it could be investigated.

If the Tables I. and II. are compared, we see that there is practically no influence of temperature upon the intensity distribution in the horizontal series. (The small irregular differences must be attributed to secondary effects.) Table II., however, shows definitely that the vertical series have the behaviour of the intensities which is postulated by the theory if they are interpreted according to assumption "*B*." It shows also that increased pressure has the same effect as increased temperature in accordance with what we expect. Goos measured only the first three lines of each band. That the higher members also behave in the right way may be seen from Kiuti's photographs of the spectrum of the hydrogen arc *. In accordance with the higher temperature of the arc, the first lines are much weakened and the higher ones enhanced, so that the fifth line is much stronger than the first one. The sixth line, which is recorded by Merton and Barratt as appearing only with the admixture of helium, has in the arc the same intensity as the first line. For a more detailed discussion of the variation of the intensity distribution with temperature the reader is referred to another paper by the writer †.

It seems that it will be very difficult, if not impossible, to account for this behaviour of the lines on the basis of assumption "*A*," and therefore" it is a very strong support for assumption "*B*."

5. *Moment of Inertia.*—Interpretation "*A*" gives a reasonable value for the moment of inertia (Curtis found $0{\cdot}186 . 10^{-40}$ for the final state of the first band). The value which was given in the author's paper (assumption "*B*") is $0{\cdot}82 . 10^{-40}$; but this value depends on the interpretation of the positive branches, which, as was already mentioned above, is still

* *Loc. cit.*

† G. H. Dieke, *Zs. f. Phys.* xxxii. p. 180 (1925).

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very uncertain. The intensity anomalies suggest that the value must be changed by a factor $\frac{1}{2}$ or $\frac{1}{4}$, but, as recent examples have shown, a secure value for the moment of inertia can only be derived from a band if its structure is *completely* known. Therefore it seems rather premature just now to discuss the various possibilities. Attention must, however, be drawn to the fact that the model of the H_2^+-ion as calculated by Pauli * and Niessen † has a much larger moment of inertia ($7{\cdot}13 \,.\, 10^{-40}$). The only thing which can be predicted about the moment of inertia of an *excited* H_2^+-molecule is that its value will lie between that of the normal molecule (as derived from specific heat data) and that of the H_2^+-ion. Although the model of Pauli and Niessen could not be verified quantitatively, a large value for an excited molecule is not unlikely. Therefore the writer cannot agree with Richardson and Tanaka's conclusion ‡ that the carrier of the band discovered by these authors must be H_3 only because of its large moment of inertia ($0{\cdot}624 \,.\, 10^{-40}$ and $0{\cdot}480 \,.\, 10^{-40}$).

6. The existing data do not yet allow us to decide with certainty how the three groups are connected. It seems, however, impossible that all the three groups are due to *one* electronic transition, but not unlikely that they must be attributed to three different electronic transitions.

If in a molecule the electric momentum has no component, or a constant one along the line joining the nuclei, according to Bohr's correspondence principle there is no possibility that a simultaneous change of the electronic configuration and the oscillation occurs. Therefore to such an electronic transition belongs only the group $\Delta n = 0$. It is possible that the bands which we have considered represent such a case. A further investigation of the bands will surely give certainty also regarding this point.

Leiden, Instituut voor theoretische Natuurkunde,
April 1925.

* W. Pauli, jun. *Ann. d. Phys.* lxviii. p. 177 (1922).
† K. F. Niessen, *Arch. Néerl.* 1923; *Ann. d. Phys.* lxx. p. 124 (1923).
‡ O. W. Richardson and T. Tanaka, Proc. Roy. Soc. A, cvi. p. 640 (1924).

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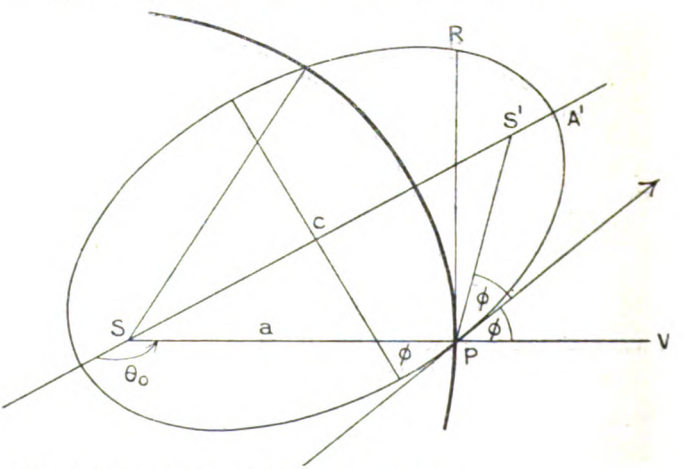
XVII. *On the Motion of a Particle projected from a point on the Earth's Surface—Variation in Gravity being taken into account. By* JAMES ROBERTSON, *M.A., B.Sc., Assistant to the Professor of Natural Philosophy in the University of Glasgow* *.

THE ordinary theory of the motion of a projectile is well known and the various results—*e. g.*, time of flight, horizontal range, greatest height attained, etc.—are given in many text-books of elementary dynamics. The fundamental assumption is that the speed of projection is so small compared with the "speed from infinity" that squares and higher powers of the ratio of these two speeds may be entirely neglected. The object of the present paper is to extend the analysis to the case of great speed of projection, *i. e.* where the height attained is so great that variations in gravity must be taken into account. I do not think the results obtained have been explicitly given before.

Let the particle be projected from the point P on the earth's surface with a speed v, the direction of projection making an angle ϕ with the vertical (SPV) at P.



The differential equation to be solved is

$$\frac{d^2u}{d\theta^2}+u=\frac{\mu}{h^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where the symbols have their usual meanings.

* Communicated by the Author.

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For the earth's attraction $\mu = ga^2$, where a is the earth's radius; also h, the constant angular momentum about S, is seen from the circumstances of projection to be $av \sin \phi$. Hence (1) becomes

$$\frac{d^2u}{d\theta^2} + u = \frac{1}{2H \sin^2 \phi}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where H is written for $v^2/2g$.

The energy equation connecting the velocity V at any distance r with the major axis 2α of the orbit of the particle is

$$V^2 = \mu\left(\frac{2}{r} - \frac{1}{\alpha}\right). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Inserting the condition that $V = v$ when $r = \frac{1}{u} = a$, we get

$$\alpha = \frac{ga^2}{2ga - v^2} = \frac{a^2}{2(a - H)}. \quad . \quad . \quad . \quad . \quad (4)$$

The first integral of (1) is

$$\frac{1}{2}\left\{\left(\frac{du}{d\theta}\right)^2 + u^2\right\} = \frac{u}{2H \sin^2 \phi} + C, \quad . \quad . \quad . \quad (5)$$

where the value of the constant C is determined from the condition that $r d\theta/dr = \tan \phi$ when $r = a$. Thus we find that $C = -\frac{\operatorname{cosec}^2 \phi}{2a^2 H}(a - H)$. Hence (5) becomes

$$\left(\frac{du}{d\theta}\right)^2 = \frac{u}{H}\operatorname{cosec}^2 \phi - \frac{a - H}{a^2 H}\operatorname{cosec}^2 \phi - u^2, \quad . \quad . \quad (6)$$

which may be written

$$\left(\frac{du}{d\theta}\right)^2 = \frac{\operatorname{cosec}^4 \phi}{4H^4} - \frac{a - H}{a^2 H}\operatorname{cosec}^2 \phi - \left(u - \frac{\operatorname{cosec}^2 \phi}{2H}\right)^2. \quad (6')$$

The apsidal distances are given by the values of u for which $\frac{du}{d\theta} = 0$.

Thus for the discussion of the highest point attained by the particle above the earth's surface we require the smaller root u_1 of the quadratic obtained by putting the right-hand side of (6′) $= 0$.

Thus

$$u_1 = \frac{\operatorname{cosec}^2 \phi}{2H} - \frac{\operatorname{cosec}^2 \phi}{2H}\sqrt{1 - 4\frac{H}{a}\left(1 - \frac{H}{a}\right)\sin^2 \phi}. \quad (7)$$

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In the figure $SA' = \frac{1}{u_1}$,

$$i.e. \quad SA' = \frac{a}{2} \frac{1 + \sqrt{1 - 4\frac{H}{a}\left(1 - \frac{H}{a}\right)\sin^2\phi}}{1 - \frac{H}{a}} \quad . \quad . \quad . \quad (8)$$

If e is the eccentricity of the elliptic path,

$$SA' = \alpha(1+e) = \frac{a}{2\left(1 - \frac{H}{a}\right)}(1+e) \text{ from (4).}$$

Hence

$$e = \sqrt{1 - \frac{4H}{a}\left(1 - \frac{H}{a}\right)\sin^2\phi} \quad . \quad . \quad (9)$$

When this expression for e is developed in powers of H/a not above the third, we find on putting $H = v^2/2g$,

$$e = 1 - \frac{v^2}{ga}\sin^2\phi + \frac{v^4}{2g^2a^2}\sin^2\phi\cos^2\phi + \frac{v^6}{2g^3a^3}\sin^4\phi\cos^2\phi + \ldots . \quad . \quad . \quad (10)$$

The greatest height attained is $SA' - a$.

From (8) we obtain after reduction and expansion

$$SA' - a = H\cos^2\phi\left\{1 + \frac{H}{a}(1 + \sin^2\phi) + \frac{H^2}{a^2}(1 + \sin^2\phi + 2\sin^4\phi) + \ldots\right\}.$$

Calling this height H', putting $H = v^2/2g$, and writing θ for the angle which the direction of projection makes with the horizontal through P, we obtain, corresponding to a result of elementary dynamics:

$$H' = \frac{v^2\sin^2\theta}{2g}\left\{1 + \frac{v^2}{2ga}(1 + \cos^2\theta) + \frac{v^4}{4g^2a^2}(1 + \cos^2\theta + 2\cos^4\theta) + \ldots\right\}. \quad (11)$$

Note that $2ga$ is the square of the "velocity from infinity," so that the assumption made in the ordinary elementary case is that squares and higher powers of $(v^2/2ga)$ are to be neglected.

If e. g. v is of the order of 3000 f./s., (11) would become

$$H' = \frac{v^2\sin^2\theta}{2g}\left\{1 + \cdot 0066(1 + \cos^2\theta) + \cdot 000044(1 + \cos^2\theta + 2\cos^4\theta) + \ldots\right\}. \quad (12)$$

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Reverting again to the figure,

$$S'A' = \alpha(1-e) = \frac{a^2(1-e)}{2(a-H)},$$

and if this be developed in powers of v^2/ga we get

$$S'A' = \frac{v^2\cos^2\theta}{2g}\left\{1+\frac{v^2}{2ga}\cos^2\theta+\frac{v^4\cos^2\theta}{4g^2a^2}(1-2\sin^2\theta)\ldots\right\}. \quad . \quad . \quad . \quad (13)$$

If all but the first term of this last expansion be neglected, we get that the distance from the nearer focus to the highest point is $v^2\cos^2\theta/2g$. Now in the case of the slowly moving projectile the equation of the path referred to tangent and normal through the vertex is $x^2 = \frac{2v^2\cos^2\theta}{g}y$, *i. e.* the "parameter" of the parabola is $\frac{2v^2\cos^2\theta}{g}$.

The results (10) and (13) show that when a particle is projected from a point on the earth's surface the path is really an ellipse, but that when the speed of projection is relatively small the part of the ellipse above the earth's surface is not much different from a parabola. Only if gravity were constant would the path be an exact parabola.

Reverting to (6′), this equation gives on integration

$$\theta-\alpha = \cos^{-1}\left[\frac{2aHu-a\operatorname{cosec}^2\phi}{a\operatorname{cosec}^2\phi\sqrt{1-\frac{4H}{a}\left(1-\frac{H}{a}\right)\sin^2\phi}}\right] \quad (14)$$

in terms of the original data H and ϕ, or using the value of e already obtained,

$$2Hu\sin^2\phi = 1+e\cos(\theta-\alpha). \quad . \quad . \quad . \quad (15)$$

Now from the triangle SPS′,

$$SP = a, \quad PS' = 2\alpha-a = \frac{aH}{a-H},$$

and

$$\frac{\sin\theta_0}{\frac{aH}{a-H}} = \frac{\sin 2\phi}{\frac{a^2e}{a-H}};$$

$$\therefore \quad \sin\theta_0 = \frac{H}{ae}\sin 2\phi.$$

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From (9) we get

$$a^2e^2 = a^2 - 4\mathrm{H}a\left(1-\frac{\mathrm{H}}{a}\right)\sin^2\phi, \quad . \quad . \quad . \quad (16)$$

so that

$$a^2e^2 - 4\mathrm{H}^2\sin^2\phi\cos^2\phi = (a - 2\mathrm{H}\sin^2\phi)^2.$$

Hence we have

$$\cos\theta_0 = \sqrt{1-\frac{\mathrm{H}^2}{a^2e^2}\sin^2 2\phi} = -\frac{a-2\mathrm{H}\sin^2\phi}{ae}, \quad . \quad (17)$$

since $\theta_0 > \frac{\pi}{2}$.

Hence to find the constant α in (15) we have $\theta = \theta_0$ when $u = \frac{1}{a}$.

The final form of the equation of the orbit then becomes

$$2\mathrm{H}u\sin^2\phi = 1 + e\cos\theta. \quad . \quad . \quad . \quad . \quad (18)$$

For the time of flight,

$$h = r^2\frac{d\theta}{dt} = \frac{4\mathrm{H}^2\sin^4\phi}{(1+e\cos\theta)^2}\cdot\frac{d\theta}{dt}.$$

The time taken for the particle to encounter the earth's surface again is therefore given by

$$h\mathrm{T} = 8\mathrm{H}^2\sin^4\phi\int_{\theta_0}^{\pi}\frac{d\theta}{(1+e\cos\theta)^2}.$$

This integral can be evaluated by the substitution $u = \tan\theta/2$ or by putting

$$\cos\lambda = \frac{\cos\theta + e}{1 + e\cos\theta}.$$

Using the latter method we get

$$h\mathrm{T} = \frac{8\mathrm{H}^2\sin^4\phi}{(1-e^2)^{3/2}}\int_{\lambda_0}^{\pi}(1 - e\cos\lambda)\,d\lambda,$$

where

$$\cos\lambda_0 = -\frac{a(1-e^2) - 2\mathrm{H}\sin^2\phi}{2\mathrm{H}e\sin^2\phi}.$$

Performing the integration, we get finally

$$h\mathrm{T} = \frac{8\mathrm{H}^2\sin^4\phi}{(1-e^2)^{3/2}}\left[\tan^{-1}\left\{\frac{2\mathrm{H}\sqrt{1-e^2}.\sin\phi.\cos\phi}{a(1-e^2)-2\mathrm{H}\sin^2\phi}\right\} + \sqrt{1-e^2}.\cot\phi\right]. \quad . \quad . \quad (19)$$

To test the accuracy of this result we apply it to obtain

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the result of one of the examples proposed in Gray's 'Dynamics' (Ex. 15, p. 302). The question reads: "A particle is projected from the earth's surface so as to describe a portion of an ellipse whose major axis is 1·5 times the earth's radius. If the direction of projection makes an angle of 30° with the vertical, prove that the time of flight is $\frac{3}{4}\sqrt{\frac{3a}{g}}\left\{\tan^{-1}\sqrt{6}+\sqrt{\frac{2}{3}}\right\}$."

In this case

$$v^2=\frac{2}{3}ga,\quad e=\frac{\sqrt{7}}{3},\quad \phi=\frac{\pi}{6},$$

so that the formula of (19) gives in the present case

$$T=\frac{2\left(\frac{2}{3}ga\right)^{3/2}\left(\frac{1}{8}\right)}{g^2a\left(1-\frac{7}{9}\right)^{3/2}}\left[\tan^{-1}\left\{\frac{\frac{2}{3}ga\cdot\frac{1}{2}\cdot\frac{\sqrt{3}}{2}\cdot\frac{\sqrt{2}}{3}}{\frac{2}{9}ga-\frac{1}{6}ga}\right\}+\frac{\sqrt{2}}{3}\sqrt{3}\right],$$

and this readily gives the result required.

We next proceed to develop the expression for T in powers of v^2/ga, i.e. to give the time of flight explicitly in terms of the initial data v and ϕ.

We rewrite (19) first as

$$T=\frac{2v^3\sin^3\phi}{g^2a(1-e^2)^{3/2}}\left[\tan^{-1}\left\{\frac{v^2\sin\phi\cos\phi\sqrt{1-e^2}}{ga(1-e^2)-v^2\sin^2\phi}\right\}+\sqrt{1-e^2}\,.\cot\phi\right]. \quad (19')$$

From (9) we get

$$1-e^2=4\frac{H}{a}\sin^2\phi\,(a-H)\ ;$$

$$\therefore\ \frac{2v^3\sin^3\phi}{g^2a(1-e^2)^{3/2}}$$

$$=\frac{1}{\sqrt{2}}\sqrt{\frac{a}{g}}\left\{1+\frac{3}{2}\frac{H}{a}+\frac{15}{8}\frac{H^2}{a^2}+\frac{35}{16}\frac{H^3}{a^3}+\dots\right\}. \quad (20)$$

Similarly $\tan^{-1}\left\{\frac{v^2\sin\phi\cos\phi\sqrt{1-e^2}}{ga(1-e^2)-v^2\sin^2\phi}\right\}$ becomes on expansion in powers of H,

$$2\cos\phi\sqrt{\frac{H}{a}}\left\{1+\frac{H}{a}\left(\frac{3}{2}+\frac{4}{3}\cos^3\phi\right)+\frac{H^2}{a^2}\left(\frac{23}{8}-6\cos^3\phi\right)\dots\right\}. \quad (21)$$

Also . . .

$$\sqrt{1-e^2}\cot\phi=2\sqrt{\frac{H}{a}}\left\{1-\frac{1}{2}\cdot\frac{H}{a}-\frac{1}{8}\frac{H^2}{a^2}\dots\right\}. \quad (22)$$

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Adding (21) and (22) and multiplying by the expansion on the right of (20), we get finally

$$T = \sqrt{\frac{2H}{g}} \cos\phi \left\{ 2 + \frac{H}{a}\left(\frac{5}{2} - \frac{4}{3}\cos^3\phi\right) + \frac{H^2}{a^2}\left(\frac{49}{8} - 8\cos^3\phi\right) \dots \right\};$$

or in terms of v and θ,

$$T = \frac{v \sin\theta}{g} \left\{ 2 + \frac{v^2}{2ga}\left(\frac{5}{2} - \frac{4}{3}\sin^3\theta\right) + \frac{v^4}{4g^2a^2}\left(\frac{49}{8} - 8\sin^3\theta\right) \dots \right\} \quad . \quad . \quad . \quad (23)$$

Where $\frac{v^2}{2ga}$ is neglected, this result reduces to

$$T = \frac{2v \sin\theta}{g}.$$

If v is 3000 f./sec.,

$$T = \frac{2v \sin\theta}{g} \left\{ 1 + \cdot 0033\left(\frac{5}{2} - \frac{4}{3}\sin^3\theta\right) + \cdot 000022\left(\frac{49}{8} - 8\sin^3\theta\right) + \dots \right\}.$$

We next wish to find the range on the horizontal plane through the point of projection.

The equation of the orbit referred to rectangular axes through C is

$$\frac{x^2}{\alpha^2} + \frac{y^2}{\beta^2} = 1, \quad \text{where} \quad \beta^2 = \alpha^2(1 - e^2). \quad . \quad . \quad (24)$$

The equation of the chord PR which is at right angles to SP and is the range required is

$$\frac{x - a\cos\theta_0}{-\sin\theta_0} = \frac{y - a\sin\theta_0}{\cos\theta_0} = \rho, \quad . \quad . \quad . \quad (25)$$

where ρ is the distance of (x, y) from P measured along PR.

(24) and (25) give

$$\frac{(a\cos\theta_0 - \rho\sin\theta_0)^2}{\alpha^2} + \frac{(a\sin\theta_0 + \rho\cos\theta_0)^2}{\beta^2} = 1,$$

whence

$$PR = \rho = -\frac{2ae^2\cos\theta_0 \sin\theta_0}{1 - e^2\sin^2\theta_0}.$$

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Inserting the values of $\cos\theta_0$ and $\sin\theta_0$ previously determined and expanding as before, we obtain

$$\mathrm{PR} = \frac{v^2 \sin 2\theta}{g}\left\{1 - \frac{v^2}{ga}\cos^2\theta + \frac{v^4}{4g^2a^2}\sin^2 2\theta + \ldots\right\}. \quad (26)$$

This reduces to $v^2 \sin 2\theta/g$ when the velocity is relatively small.

If $v = 3000$ f./sec.,

$$\mathrm{PR} = \frac{v^2 \sin 2\theta}{g}\left\{1 - \cdot 0132 \cos^2\theta + \cdot 000044 \sin^2 2\theta + \ldots\right\}.$$

Next compare this with the arc intercepted on the meridian, viz.

$$2a\theta_0 = 2a \sin^{-1}\left(\frac{\mathrm{H}}{ae}\sin 2\phi\right).$$

On expansion we get

$$\text{arc} = \frac{v^2 \sin 2\theta}{g}\left\{1 + \frac{v^2}{ga}\cos^2\theta + \frac{v^4}{24g^2a^2}\sin^2 2\theta + \ldots\right\}, \quad (27)$$

agreeing with the distance along the chord PR to a first approximation.

For a speed of 3000 f./sec. the difference between the chord and the arc on the meridian is $\dfrac{\cdot 0264 v^2 \sin 2\theta \cos^2\theta}{g}$, the maximum value of which is about $\cdot 0005 \,.\, v^2$ = about $\frac{9}{10}$ mile in a range of approximately 46 miles.

XVIII. *On a Method of Measurement of Newton's Coefficient of Restitution, and the Law of Oblique Impact.* By H. G. Green, *M.A., Lecturer in Mathematics, University College, Nottingham**.

THE following research was undertaken in order to find with what degree of accuracy the theoretical equations for the rebound of a sphere from a plane, whether smooth or rough, were obeyed in the case of an oblique impact. For a satisfactory investigation it was clearly essential that angles of impact and rebound could be measured with accuracy, and that during impact the sphere should be free from external restraint. The general disposition of the apparatus designed by the author to fulfil these conditions is shown in fig. 4. The sphere used was a ball of fairly soft wood through which a cylindrical hole ran

* Communicated by Prof. E. H. Barton, F.R.S.

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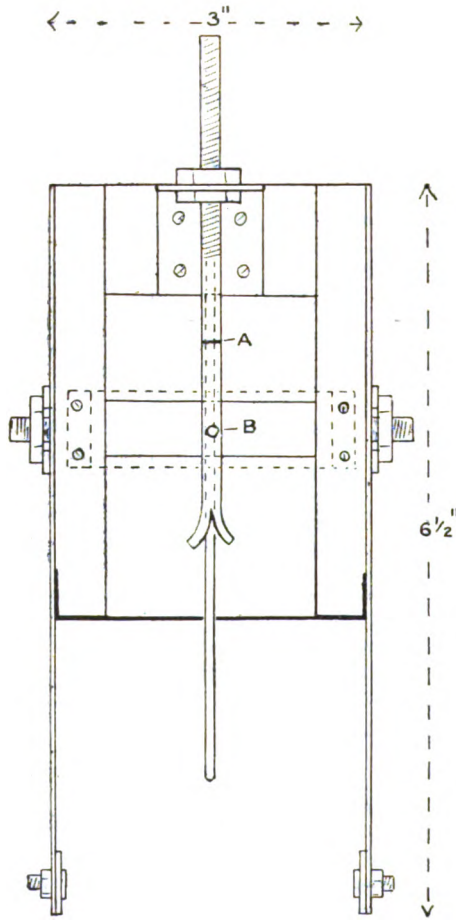
centrally of such radius that it could slide easily on the guiding-rod of the pistol (fig. 1). It was shot obliquely on to a brass plate mounted on an inclined plane, and

Fig. 1.



The pistol shown in plan.

the angle of the plane was varied until the direction of rebound was as nearly vertical as could be obtained by the means of adjustment, the ball falling back approximately to the point of impact. The angles of impact

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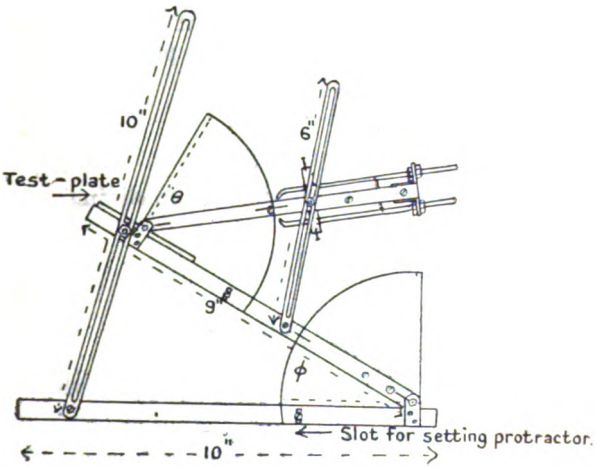
and rebound (directions from the normal), θ, ϕ as marked, were measured by means of four protractors permanently mounted on the apparatus, of which a side view is shown in fig. 2. It was found advisable, in order to obtain accurate angle measurements, to dispense with ordinary hinges at the points of measurement, and to replace them by small tightly-fitting bolts through brass plates attached to the frame of the apparatus, the protractors being carefully centred on these bolts. It was also found, to avoid strain on the guiding-rod and to secure smooth discharge, that the release system of the ball had to be double and of even action on

Fig. 2.



Sectional view of the apparatus.

both sides. The triggers consisted of two rods with curved double prongs at the extremities towards the plane, the rods being in the direction of the guiding rod. The prongs were sheathed in pieces of rubber tube to prevent damage to the ball. In order to mount a trigger, one plate of an ordinary metal hinge was fastened to the pistol frame, and the rod was fitted through a hole in the other plate. The length of the trigger could be varied by means of two nuts, which were screwed up tightly on to the hinge on either side. The two triggers were connected by a spring (A, fig. 1), and provided with screw-stops (B) on bridges over them, by means of which their ranges could be adjusted.

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Theory.

The detailed discussion of the mathematical theory for the impact of a sphere against a rough plane will be found in any text-book on Rigid Dynamics (for example, Loney, 'Dynamics of a Particle and of Rigid Bodies,' pp. 274–276).

In the case under discussion the sphere has no initial angular velocity. Let u, v be the components of velocity tangential and normal to the plane on approach, and u', v' the corresponding components after impact, a the radius, and k the radius of gyration about the central axis perpendicular to the plane of motion.

Then

$$v \tan\theta = u, \quad v' \tan\phi = u', \quad v' = ev,$$

where e is the Newton Coefficient of Restitution. For "large" values of θ where sliding takes place

$$u' = u - \mu v(1+e),$$

or since

$$v' = ev, \quad e\tan\phi = \tan\theta - \mu(1+e). \qquad \text{[Type A.]}$$

For "small" values of θ where there is no sliding

$$\left(1+\frac{k^2}{a^2}\right)u' = u,$$

or

$$\left(1+\frac{k^2}{a^2}\right)e\tan\phi = \tan\theta. \qquad \text{[Type B.]}$$

The critical angle between the cases is obtained when

$$\tan\theta = \mu(1+e)\left(1+\frac{a^2}{k^2}\right),$$

where μ is the coefficient of friction.

Experimental Procedure.

It was found convenient, in making any observation, to appoint first the angle θ and then to find the corresponding ϕ by adjustment of the inclined plane, the greater arc of the ϕ adjustment rendering it the more sensitive one. As the correct setting was approached, a considerable number of trials were made in each position so as to cut out the possibility of a false bounce. In addition, after the best position was obtained and when the readings had been observed, for further check two near settings of the plane, equally spaced from the read one, were made and the resulting ranges of the projectile on the plane noticed:

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these should be very approximately equal. The angle readings are all direct (θ, not its complement, being observed) since errors in the deduced value of e due to overestimate (or underestimate) of both θ and ϕ tend to cut out. This takes advantage of a psychological phenomenon that, in a short series of readings such as make up an observation in this case, any temporary tendency to read high will probably persist through that series. In the following tables the angle readings are the average ones.

In Experiments 1, 2, 3 (Table I.) the brass plates were very highly polished. The observations were all of type A, but with a μ too small to detect. We have, therefore, for for all intents and purposes the case of a ball impinging on a smooth plane and obeying the law $e \tan \phi = \tan \theta$.

In Experiment 4 (Table II.) the brass plate was roughened before being mounted. Experiments 5, 6 were made immediately after 2, 3 respectively, the planes being roughened with sand-paper while still mounted. This course was taken, as it was desired to notice the effect on the Coefficient of Restitution of a slight breaking up of the surface. It was found that the coefficient of the system depended not only on the plate itself, but also on the security of its fastenings, so that in any comparative experiments the fastenings had to be left undisturbed. A considerable decrease in the value of the constant was found. In deducing the numerical results of Experiments 4, 5, 6 the graphs connecting $\tan \theta$, $\tan \phi$ were first plotted (shown in fig. 3) to determine the types of the observations. The numerical values of e, $\mu(1+e)$ for type A were obtained by Gauss's Method of Mean Squares applied to the four best-spaced readings; for type B the value of e for each observation was determined directly; the critical value for θ was obtained by solution of the equations of the two lines and also by theoretical deduction from the value obtained for $\mu(1+e)$. The diameter of the sphere was ·86 inch; that of the cylindrical hole ·24 inch, leading to $k^2/a^2 = \cdot 4078$.

The degree of accuracy obtained in the experiments of Table II. was not as high as that obtained in those of Table I. In the latter case the "ϕ" readings for any setting "θ" were determined by repeated experiment, between each of which the inclined plane was moved and readjusted in the course of the next trial, the relative position of the pistol being undisturbed. This involved a very great number of impacts, and in the experiments of Table II. this number had to be reduced to minimize the wear of the plate with consequent change of μ. The two

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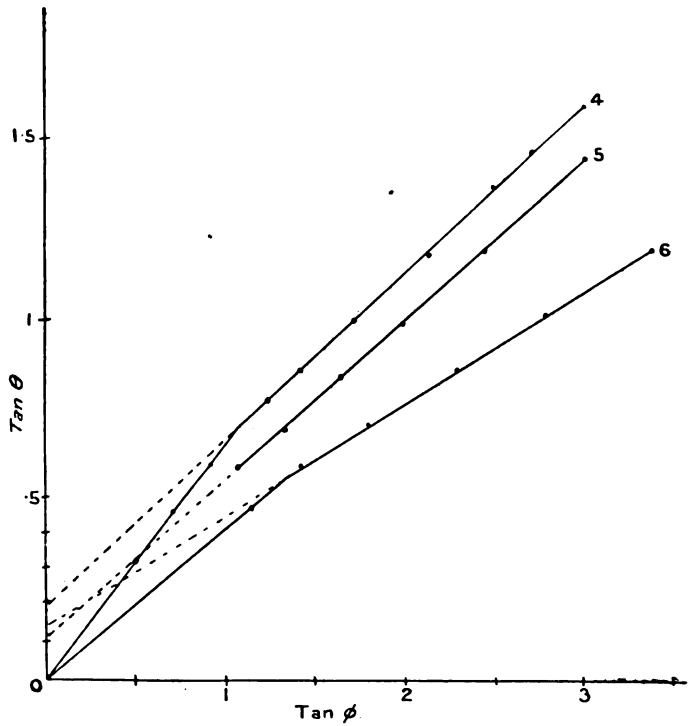
Fig. 3.



The results of experiments expressed graphically.

TABLE I.

1.			2.			3.		
$\theta°$.	$\phi°$.	*e*.	$\theta°$.	$\phi°$.	*e*.	$\theta°$.	$\phi°$.	*e*.
$61\frac{5}{8}$	74	·53085	60	$73\frac{15}{16}$	·49870			
55	$69\frac{5}{8}$	·53022	55	$70\frac{3}{4}$	·49874	55	$74\frac{1}{4}$	·40277
$50\frac{1}{8}$	$66\frac{1}{4}$	·52983	$50\frac{5}{16}$	$67\frac{1}{2}$	·49914	50	$71\frac{3}{8}$	·40165
$45\frac{1}{4}$	$62\frac{1}{4}$	·53073	$45\frac{7}{16}$	$63\frac{5}{8}$	·49912	45	$68\frac{1}{8}$	·40149
40	$57\frac{3}{4}$	·52943	40	$59\frac{1}{4}$	·49922	40	$64\frac{3}{8}$	·40233
$34\frac{3}{4}$	$52\frac{1}{2}$	·53007	$35\frac{1}{8}$	$54\frac{3}{4}$	·49946	35	$60\frac{1}{8}$	·40224
30	$47\frac{1}{2}$	·52904	30	$49\frac{1}{8}$	·49967	30	$55\frac{1}{8}$	·40239
			25	$43\frac{1}{8}$	·49855	25	$49\frac{1}{4}$	·40180
Average		·5300	Average		·4991	Average		·4021

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TABLE II.

	4.		5.		6.	
	$\theta°$.	$\phi°$.	$\theta°$.	$\phi°$.	$\theta°$.	$\phi.°$
Type A	58 56 54 50 45 $40\frac{1}{5}$ 38	$71\frac{1}{2}$ $69\frac{7}{8}$ $68\frac{1}{4}$ *65 $59\frac{3}{4}$ $54\frac{15}{16}$ $51\frac{1}{8}$	55 50 45 40 35 $30\frac{1}{2}$	$71\frac{3}{4}$ $67\frac{3}{4}$ 64 $58\frac{3}{4}$ $53\frac{1}{8}$ $47\frac{1}{2}$	$50\frac{1}{8}$ 45 40 35 30	$73\frac{1}{5}$ $70\frac{1}{8}$ $66\frac{1}{8}$ $60\frac{15}{16}$ 54
Type B	$30\frac{1}{5}$ $25\frac{3}{4}$ $20\frac{1}{8}$	$42\frac{1}{2}$ $35\frac{2}{5}$ 29		†	25	48
e from Type A.	·470		·437		·299	
e from Type B.	·467				·298	
$\mu(1+e)$	·197		·125		·157	
Critical θ (theory).	$\tan^{-1}$ ·682		$\tan^{-1}$ ·430		$\tan^{-1}$ ·543	
" " (intersect. of lines).	$\tan^{-1}$ ·693				$\tan^{-1}$ ·548	

* The graph shows this to be a faulty reading.

† No readings of Type B were obtainable.

values for the critical angle (Table II.) are not completely independent. The theoretical expression is that which satisfies the theoretical equations, and its numerical result is the one which would be obtained if the Type B value for e were taken as exactly equal to the Type A value; the closeness of these results is a severe test on the accuracy of the method. The same table also illustrates a drawback to the method, which is unsatisfactory for impacts near the normal. The last angles in each set are the least for which satisfactory definition could be obtained.

The close adherence of the results to the two linear laws and the near equality of the values of "Newton's Constant" deduced from these laws justify the assumptions that, within the ranges of tangential and normal velocities employed, μ and e have constant values, and confirms the resulting

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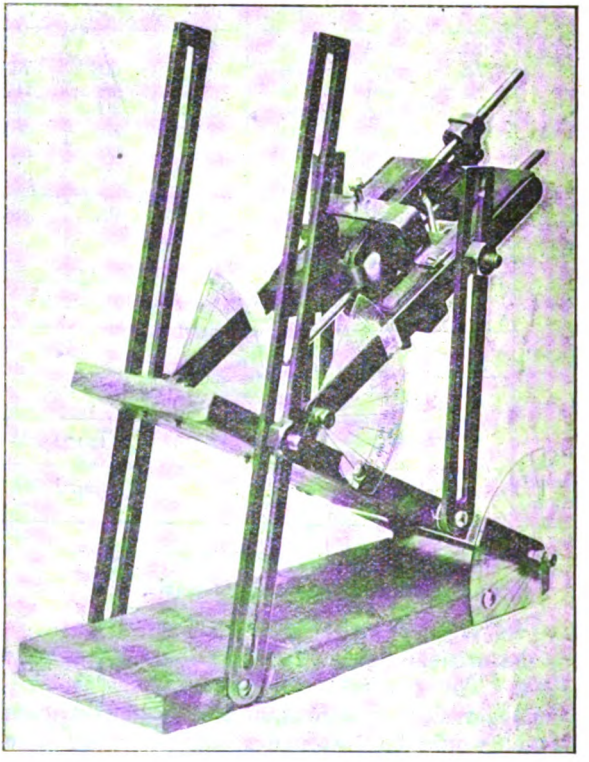
dynamical equations for the behaviour of a sphere impinging on a rough plane.

Fig. 4.



General view of the apparatus used for impact experiments.

Summary.

An apparatus is described by which the coefficient of restitution between a plane and a sphere can be obtained to a considerable degree of accuracy. Impacts of a sphere with smooth and rough planes are dealt with, and the theoretical equations are shown to be very closely satisfied.

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XIX. *On an Extension of the Negative Band Spectrum of Nitrogen.* By T. R. MERTON, *F.R.S.*, and J. G. PILLEY, *B.A.**

WE have recently described (Roy. Soc. Proc. A cvii. p. 411, 1925) observations of the spectrum of Nitrogen which is produced when discharge-tubes containing a very small proportion of nitrogen in helium at comparatively high pressures are excited by condensed discharges of moderate intensity. Under these conditions the arc spectrum is isolated, and it was pointed out that in the presence of helium the negative bands were enhanced at the expense of the positive bands. We have now further investigated the discharge conditions which are most favourable to the isolation of the negative bands. These experiments have not only facilitated a remeasurement of the known band heads, but have also made it possible to observe an extension of the bands into the less refrangible parts of the spectrum. Measurements of the heads of the bands recognized are summarized in Kayser's 'Handbuch der Spectrographie,' vol. v., the most reliable of these being probably those given by Deslandres (*Comptes Rendus*, cxxxix. p. 1174, 1904), who has arranged the heads of the bands into six series. Deslandres' assignment of the different bands into these series seems to have depended to some extent on the general appearance of the bands, for the members of the series do not show constant second differences in the wave-numbers, and his arrangement therefore seems to merit some further consideration. These discrepancies seem to be due in part to a confusion with the bands of the positive system, and many of the bands are so weak under ordinary conditions that their identification is almost impossible.

According to recent developments in the application of the quantum theory to band spectra, the heads of bands are points of no special theoretical significance, but they nevertheless serve in the arrangement of the different bands into series, and a knowledge of their wave-lengths is of importance for purposes of identification in celestial spectra. In particular the negative bands of nitrogen constitute an important part of the spectrum of the aurora. The appearance of the bands in the aurora and under different conditions in the

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laboratory has been studied by Rayleigh (Roy. Soc. Proc. A, ci. p. 114, 1922). Rayleigh found that the distribution of intensity in the bands in the auroral spectrum more closely resembled that seen in the positive column in discharge-tubes at low pressures than that seen in the negative glow and first negative layer, though in the latter sources the negative bands were more completely (though not entirely) isolated from the positive system.

The preparation of the discharge-tubes used in the experiments here recorded has been described in a previous investigation (*loc. cit.*). When these tubes, which contained helium at pressures about 30 mm. of mercury and a trace of nitrogen, and which were provided with wide tubes in place of the usual capillary, were excited by uncondensed discharges the negative bands were very much more prominent than in tubes containing pure nitrogen. It is well known that in vacuum-tubes containing pure nitrogen the negative bands are enhanced at very low pressures and appear strongly throughout the tubes. With feebly condensed discharges our tubes show an even greater enhancement of the negative bands, but in the course of a series of experiments to discover the optimum conditions for the isolation of the bands it was found that when the tubes were excited by a high frequency discharge from a small Tesla coil the positive bands very nearly disappeared, and it was moreover evident that further members of the negative band system could be traced into the less refrangible parts of the spectrum. All the negative bands could be seen clearly and distinctly, and these conditions seemed appropriate to a remeasurement of the spectrum. A preliminary examination showed that such a remeasurement was essential to an arrangement of the heads of the bands. The spectrum was photographed with the concave grating instrument and the Littrow glass spectrograph described in the previous investigation (*loc. cit.*), and the iron arc served as a comparison spectrum. It must be borne in mind that a high degree of precision cannot be attained in the measurement of the heads of unresolved bands, and the wave-lengths are accordingly given to the nearest tenth of an ångström. The results are given in Table I., in which the wave-lengths are given in comparison with those of previous investigators. The intensities in the tubes containing helium and nitrogen with the Tesla excitation are also compared with those observed with a wide bore tube containing nitrogen and excited by a discharge of moderate intensity.

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TABLE I.

λ(I.A.).	Series.	Intensity. (He+N)	Intensity. (N)	Deslandres.	Hasselberg.	Ångström.	Hemsalech.
5864·7	1	4	0				
5653·1	3	4	1				
5564·1	4	1	0				
5485·5	5	5	0				
5330·4	?	2	0				
5228·3	1	7	2	...	...	5227·5	
5148·8	2	4	3	...	...	5150·0	
5076·6	3	7	1				
5012·7	4	3	1C				
4957·9	5	5	1C				
4881·9	?	5	0				
4709·2	1	4	2	...	4708·6	4709·5	
4651·8	2	4	1	...	4651·2	4653·5	
4599·7	3	6	2	...	4599·4	4601·2	
4554·1	4	4	0	...	4553·8	4555·2	
4515·9	5	6	0	...	4515·3	4516·5	
4490·3	6	2	1	...	4484·9		
4278·1	1	8	6	...	4278·0	4281·0	4278·4
4236·5	2	7	5	...	4236·3	4239·0	4236·8
4201·1	?	4	4				
4199·1	3	4	2	...	4198·7	4203·0	4198·8
4166·8	4	3	0	...	4166·4	4175·0	4166·6
4140·5	5	2	—				
3914·4	1	6	6	3914·4	...	...	3914·4
3884·3	2	3	1	3883·9	...	...	3884·2
3857·9	3	2	2	3857·1	...	...	3857·1
3835·4	4	1	1				
3818·1	5	1	0				
3582·1	2	4	3	3581·5			
3563·9	3	4	0	3563·5			
3548·9	4	3	C	3548·2			
3538·3	5	2	C				
3532·6	6	1	0C				
3368·0	3	2	1				
3298·7	4	3	1	3298·5			
3293·4	5	3	0	3296·1			

C denotes a head much confused with other bands.

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In Table II. the assignment of the heads into series is given, the wave-numbers *in vacuo* being arranged in columns and the first and second differences being also given. Our results do not agree well with those of Deslandres, but the constancy of the second differences in our wave-numbers

TABLE II.

Series.	Wave-length in air.	Wave-number *in vacuo*.	1st diff.	2nd diff.
1	5864·7	17046·5		
	5228·3	19121·6	2075·1	
	4709·2	21229·2	2107·6	32·5
	4278·1	23368·3	2139·1	31·5
	3914·4	25539·5	2171·2	32·1
2	5148·8	19422·0		
	4651·8	21491·1	2069·1	
	4236·5	23597·7	2106·6	37·5
	3884·3	25737·4	2139·7	33·1
	3582·1	27908·8	2171·4	31·7
3	5653·1	17684·4		
	5076·6	19692·8	2008·4	
	4599·7	21734·4	2041·6	33·2
	4199·1	23807·8	2073·4	31·8
	3857·9	25913·5	2105·7	32·3
	3563·9	28051·3	2137·8	32·1
	3308·0	30221·5	2170·2	32·4
4	5564·1	17967·5		
	5012·7	19944·2	1976·7	
	4554·1	21952·0	2007·8	31·1
	4166·8	23992·3	2040·3	32·5
	3835·4	26065·4	2073·1	32·8
	3548·9	28169·8	2104·4	31·3
	3298·7	30306·7	2136·9	32·5
5	5485·5	18224·9		
	4957·9	20164·1	1939·2	
	4515·9	22137·6	1973·5	34·3
	4140·5	24144·7	2007·1	33·6
	3818·1	26183·5	2038·8	31·7
	3538·3	28254·2	2070·7	31·9
	3293·4	30355·5	2101·3	30·6

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is much closer than in the case of Deslandres' values, and it may be surmised that the recognition of the true heads of some of the bands is extremely difficult unless a comparison is made of spectra under two different conditions in one of which the negative band system is very strongly accentuated. A word must be said about the nature of the Tesla excitation. It seems possible that the chief virtue of this method lies in providing a condition intermediate between the uncondensed discharge and a condensed discharge with a very small spark-gap, but there are certain changes in spectra which seem to be peculiar to this excitation. Vegard (Phil. Mag. xivi. No. 271, p. 193, 1923) has given a summary of his measurements of the auroral spectrum and has attempted to identify a number of the lines observed with lines of the spark spectrum of nitrogen. These lines have been compared with the extension of the nitrogen bands observed in this investigation, but there appears to be no systematic agreement. At the same time it would appear that Vegard's identification with the spark spectrum seems hardly justified in view of the fact that most of the lines with which they are identified are relatively faint, and do not appear to be selectively enhanced under any known conditions of excitation. It may be mentioned that a comparison has also been made with unidentified radiations observed in the spectrum of Comet Morehouse by de la Baume Pluvinel and Baldet (Astrophys. Journ. vol. xxxiv. p. 88, 1911), but here again there appears to be no correspondence.

We wish to record our thanks to the Department of Scientific and Industrial Research for a grant made to one of us (J. G. P.) during the course of this investigation.

Winforton House, Hereford,
March 10th, 1925.

XX. *The Flow of Water in a Corrugated Pipe.* *By* Professor A. H. Gibson, *D.Sc.**

Introduction.

THE author recently had occasion to measure the loss of head in a copper pipe whose walls were corrugated circumferentially. The results showed that the loss of head was proportional to $v^{2\cdot135}$. The case of non-accelerated flow in which the index of v is greater than two is unusual, and

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although results of tests on pipes have occasionally been published indicating such an index, no such case has hitherto come before the notice of the author. It is both of practical importance and philosophical interest, since, if the theory of dimensional similarity holds for such a state of flow, the loss of head should be diminished if the viscosity of the fluid is increased. The experiments were therefore extended with a view of investigating this point.

Experiments.

The experimental pipe is of smooth drawn copper. The internal diameter at the bottom of the corrugations is 1·80 in. and at the top 2·0 in. Each corrugation takes approximately the form of a sine curve 0·4 in. pitch from crest to crest. The pressure drop along the pipe was obtained from pressure orifices drilled at the tops and at the bottoms of the corrugations. The difference in pressure between the top and bottom of a corrugation was also measured in a number of tests. All pressure differences were measured on an inverted U-tube water-gauge. The majority of the experiments were carried out with water at 15°·3 C. Two series were afterwards carried out at 51°·7 C. and 73°·3 C.

Tests at Normal Temperature.

The results of the tests are shown in Table I. and in the curve of fig. 1. The velocities (computed on the

TABLE I.

Temp. 15°·3 C.

Expt.		1.	2.	3.	4.	5.	6.	7.	8.	9.
(p_1-p_2) ft.	at top	·00288	·00630	00824	·01236	·0222	·0247	·0433	·0610	·0848
	at bottom	·00288	·00630	·00824	·01230	·0220	·0240	·0422	·0595	·0824
v f.s. at enlarged section.		·513	·735	·866	1·066	1·380	1·470	1·862	2·22	2·60
Expt.		10.	11.	12.	13.	14.	15.	16.	17.	
(p_1-p_2) ft.	at top	·1296	·230	·285	·327	·428	·650	·763	1·000	
	at bottom	·1260	·222	·274	·315	·413	·618	·730	·952	
v f.s. at enlarged section.		3·19	4·16	4·53	4·90	5·52	6·65	7·15	8·12	

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TABLE I. (*continued*).

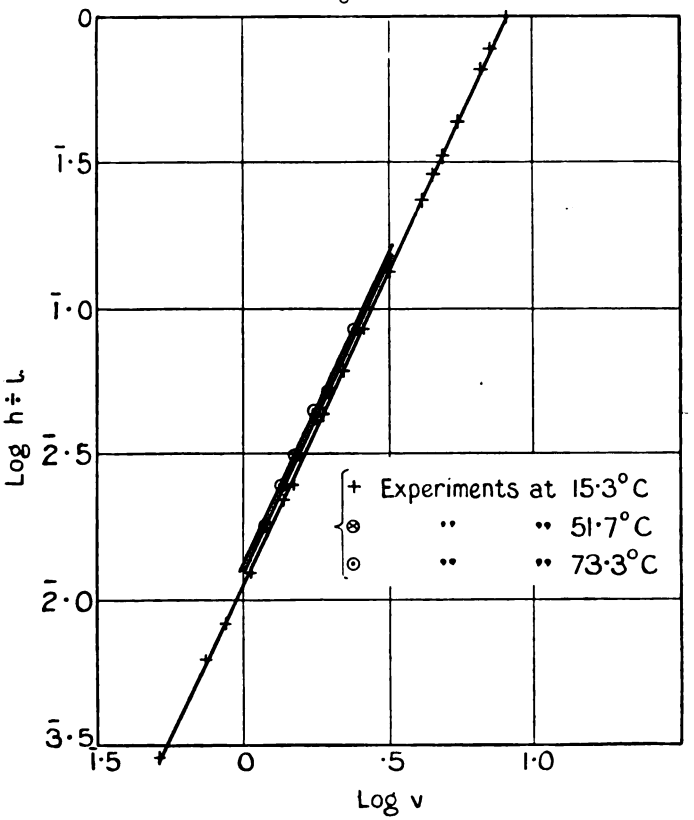
Temp. 51°·7 C.

Expt.	1.	2.	3.
$(p_1 - p_2)$ ft. at enlarged section	·0181	·0429	·0515
v f.s. at enlarged section.....	1·291	1·800	1·955

Temp. 73°·3 C.

Expt.....	1.	2.	3.	4.
$(p_1 - p_2)$ ft. at enlarged section	·02455	·0310	·0439	·0824
v f.s. at enlarged section.....	1·350	1·505	1·769	2·425

Fig. 1.



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diameter of the tube at the top of the corrugations) range from 0·5 f.s. to 8·1 f.s. On plotting the logarithms of log head against log velocity on a large scale, it appears that over this range the loss of head is proportional to $v^{2\cdot135}$, and is given by

$$h = \cdot0113\, v^{2\cdot135} \text{ ft. per foot run of pipe}$$

if the pressures are taken at the enlarged sections, and by

$$h = \cdot0113\, v^{2\cdot120}$$

if the pressures are taken at the bottom of the corrugations.

For comparison, data were also obtained for plain smooth drawn copper pipes having diameters of 1·8 in. and 2·0 in., or respectively the same as the diameters at the bottom and top of the corrugations in the corrugated pipe. The loss of head in these parallel pipes is given by

$$h = \cdot0030\, v^{1\cdot80} \text{ ft. per foot run in the 1·8 inch pipe}$$

and

$$h = \cdot0026\, v^{1\cdot80} \text{ ,, ,, ,, 2·0 ,, ,,}$$

The comparative losses of head per foot run at velocities of 1, 2, and 4 f.s. are shown in the following table :—

Pipe.	Velocity f.s.		
	1·0.	2·0.	4·0.
Corrugated pipe (vel. at large section).	·0113	·0496	·218
Ditto (vel. at small section)	·0074	·0324	·142
2·0 in. parallel pipe	·0026	·0091	·0317
1·8 ,, ,, ,, ...	·0030	·0105	·0366

The results show that the resistance of the corrugated pipe is much greater even than that of a smooth pipe having the same diameter as the contracted section of the corrugations. At 1 f.s. it is 2·5 times as great, and the effect becomes relatively greater at higher velocities.

The loss of head in such a pipe may be looked upon as being mainly due to the shock and eddy formation caused by the enlargements and contractions of section which take place throughout its length. It is known that the loss due to a sudden enlargement is given approximately by

$$\frac{(v_1 - v_2)^2}{2g} \text{ ft.,}$$

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where v_1 and v_2 are respectively the higher and lower velocities. There are 30 enlargements per foot run of the pipe, so that with a velocity of 1 f.s. in the larger sections, corresponding to 1·235 f.s. at the bottom of the corrugations, the loss per foot run, if the enlargements were sudden, would be

$$\frac{(1{\cdot}235-1{\cdot}00)^2}{2g} \times 30 = {\cdot}0256 \text{ ft.}$$

The actual loss per foot run (·0113 ft.) is 44 per cent. of this. The corresponding values at 2 f.s. and 4 f.s. are 48·5 per cent. and 53·4 per cent. This would tend to indicate that as the velocity is increased, the type of flow gradually changes, the water in the corrugations taking part to an increasiug degree in the general flow.

Confirmation of this is obtained from pressure readings at adjacent points in the crest and trough of a corrugation, for assuming the loss between a trough and the adjacent crest to be due to a reduction in velocity corresponding to the cross section of the pipe, the pressure at the enlarged section should be the greater by an amount theoretically equal to

$$\frac{v_1^2-v_2^2-(v_1-v_2)^2}{2g} \text{ ft.}$$

Thus in experiment 12, $v_1=5{\cdot}60$, $v_2=4{\cdot}53$, so that the theoretical difference in pressure would be

$$\frac{31{\cdot}4-20{\cdot}5-(1{\cdot}14)}{64{\cdot}4} \text{ ft.} = {\cdot}151 \text{ ft.}$$

The measured difference is ·094 ft., or ·625 of its theoretical value. Similarly in experiment 15, with $v_2=6{\cdot}65$ f.s., the measured difference in pressure is ·78 of the theoretical, and in experiment 16, when $v_2=7{\cdot}15$ f.s., it is ·83 of the theoretical value.

Tests at different Temperatures.

It may readily be shown from the principle of dynamical similarity that the loss of pressure "p" per unit length of a pipe conveying a virtually incompressible fluid should be given by

$$p \propto \rho v^2 \left(\frac{\nu}{vd}\right)^{2-n},$$

where ρ is the density of the fluid,
ν „ kinematic viscosity.

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This indicates that if n is greater than 2 the resistance will diminish if the viscosity is increased, and in order to investigate this point further tests were carried out in which the mean temperature of the water in the pipe was respectively 51°·7 C. and 73°·3 C.

At these temperatures the following are the values of μ, ρ, and ν :—

Series.	Temp. 0° C.	Coeff. of Viscosity.	ρ.	$\frac{\mu}{\rho} = \nu$.
1	15°·3	·0114	·999	·01142
2	51°·7	·0055	·987	·00557
3	73°·3	·0039	·977	·00399

For the experiments in which the pressure-drop at the tops of the corrugations was taken, $n = 2·135$, so that, at any given velocity, and with different temperatures,

$$\frac{p_2}{p_1} = \frac{\rho_2}{\rho_1}\left(\frac{\nu_1}{\nu_2}\right)^{·135}.$$

If $T_2 = 51°·7$ and $T_1 = 15°·3$:

$$\frac{p_2}{p_1} = \frac{·987}{·999}\left(\frac{·01142}{·00557}\right)^{·135} = 1·089\ ;$$

while if $T_3 = 73°·3$ and $T_1 = 15°·3$,

$$\frac{p_3}{p_1} = \frac{·977}{·999}\left(\frac{·01142}{·00557}\right)^{·135} = 1·128.$$

The logs of head and velocity for the experiments at these temperatures (Table I.) have been plotted to a large scale and on the same sheet. From these it appears that the measured loss of head at 51°·7 C. is 8·3 per cent. greater, and at 73°·3 C. is 12·7 per cent. greater than at 15°·3 C.

The experiments thus confirm the fact, indicated by dimensional theory, that in a pipe in which the resistance to flow increases at a greater rate than the square of the velocity, the resistance is diminished if the viscosity of the fluid is increased. The rate of diminution is also in accordance with the dimensional theory.

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XXI. *The Determination of the Best Linear Relationship connecting any Number of Variables.* By H. GLAUERT, *M.A.**

IF it is anticipated that two observed quantities x and y are connected by a linear relationship, it is customary in the theory of correlation to determine two lines of regression,

$$y = m_1 x + c_1,$$
$$x = m_2 y + c_2,$$

by the standard methods of the combination of observations. In this process the errors of observation are assumed in turn to be wholly on the variable y and wholly on the variable x. Frequently, however, it is necessary to determine the best linear relationship connecting the observed quantities, and the following method is suggested, which is applicable to any number of variables.

Consider an experiment in which m variables $x, y \ldots$ are determined by observation with equal probable error $\pm\epsilon$, in association with n variables $u, v \ldots$ whose values are known accurately in each experiment. Let $\xi, \eta \ldots$ be the true values of the first set of variables satisfying the linear relationship

$$F = \Sigma a\xi + \Sigma \alpha u = a\xi + b\eta + \ldots + \alpha u + \beta v + \ldots = 0.$$

The probable value of F, when the observed values are inserted, is

$$F(x, y \ldots u, v \ldots) = \pm \epsilon a \pm \epsilon b \ldots$$
$$= \pm \epsilon \sqrt{\Sigma a^2},$$

where the summation extends over the coefficients $a, b \ldots$ but not over the coefficients $\alpha, \beta \ldots$. Equations of equal weight are obtained by writing this result in the form

$$\frac{\Sigma ax + \Sigma \alpha u}{\sqrt{\Sigma a^2}} = \pm \epsilon,$$

and the sum of the squares of the errors is

$$S = \sum \frac{(\Sigma ax + \Sigma \alpha u)^2}{\Sigma a^2}.$$

The best linear relationship connecting the variables will be that which makes the sum S a minimum, and so the

* Communicated by Prof. A. S. Eddington, F.R.S.

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normal equations for solving the problem are of the form

$$\Sigma(\Sigma ax+\Sigma\alpha u)\{x\Sigma a^2-a(\Sigma ax+\Sigma\alpha u)\}=0$$

and $$\Sigma(\Sigma ax+\Sigma\alpha u)u=0.$$

Now put

$$X=a[xx]+b[xy]+\ldots+\alpha[xu]+\ldots,$$
$$U=a[xu]+b[yu]+\ldots+\alpha[uu]+\ldots,$$

and then

$$S=\frac{\Sigma aX+\Sigma\alpha U}{\Sigma a^2},$$

while the typical normal equations become

$$X-aS=0$$

and $$U=0.$$

There are m normal equations of the first type and n of the second type, so that in all there are $(m+n)$ equations to determine the quantity S and the $(m+n-1)$ ratios of the coefficients of the linear relationship. On eliminating the coefficients from the normal equations, a determinantal equation of degree m is obtained for S, namely

$$\begin{vmatrix} [xx]-S & [xy] & \ldots & [xu]\ldots \\ [xy] & [yy]-S & \ldots & [yu]\ldots \\ \cdot & \cdot & \cdot & \cdot \\ [xu] & [yu] & \ldots & [uu]\ldots \\ \cdot & \cdot & \cdot & \cdot \end{vmatrix}=0.$$

No ambiguity arises in the solution, since the smallest positive value of S is required, and when this value of S is inserted in the normal equations, the coefficients of the linear relationship are uniquely determined. Since S is a small quantity for good observational data, it is frequently sufficient to retain only the first power of S in expanding the determinant.

It is of interest to note the connexion between the general solution and the lines of regression when there are two variables x and y and one parameter u.

The normal equations in this case are :

$$([xx]-S)a+[xy]b+[xu]\alpha=0,$$
$$[xy]a+([yy]-S)b+[yu]\alpha=0,$$
$$[xu]a+\quad[yu]b\quad+[uu]\alpha=0,$$

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and the two lines of regression correspond exactly to the neglect of S in the first and second of these equations respectively. Geometrically, the lines of regression are derived by measuring the distance of an observed point from the line parallel to one or other of the coordinate axes, while the generalized solution depends on measuring the distance normal to the line.

XXII. *A further Note on the Forsythe Method of comparing Inductance and Capacity* *. *By* R. L. Edwards †.

In the January Philosophical Magazine, Prof. Ganguli adversely criticised the Forsythe method of comparing inductance and capacity, both from the standpoint of accuracy and sensibility. The objections are not inherent in the method, but arose in Prof. Ganguli's work as a result of his neglecting the ohmic resistance of the coils compared. That is, his $r \neq Q$, which prevented the existence of a null point. His attempt to reduce error due to this source, led him to use very high resistances. Experience in these tests, as well as theory, shows that with high resistances, low sensibility is inevitable, even though a correspondingly high resistance receiver is used. Large values of r necessitate excessively small values of C, as for a given inductance C varies inversely as r^2 for a balance. With $r = Q$, and of suitable magnitude, we obtain a very sharp null point in our work.

Our data, obtained with a thousand-cycle microphone hummer, a Brooks Inductometer, standard mica condensers, and adjustable receivers tuned to 1000 cycles, yield results with an error of less than a fifth of a percent. over the range of the inductometer. Obviously, we are not concerned with what portion of Q is within the inductive coil itself.

The shifting of resistance between s and Q and r is a tedious process, which might be greatly simplified by a potentiometer arrangement. This difficulty is averted, however, by the use of a variable standard of capacity (or inductance).

The State University of Iowa.
April 8, 1925.

* The Physical Review, Second Series, vol. i. p. 463 (1913).
† Communicated by the Author.

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XXIII. *The Scattering of Beta-Rays.* By J. CHADWICK, *Ph.D., Fellow of Gonville and Caius College, Cambridge, and* P. H. MERCIER, *D. ès S., Lausanne* *.

§ 1.

THE phenomenon of the scattering of charged particles in their passage through matter has been of great importance in the development of atomic physics. As is well known, it was from consideration of the scattering of α-particles through large angles that Rutherford was led to the conception of the nuclear atom and the theory of single scattering. In single scattering the deflexion of a charged particle through a certain angle is due to an encounter with a single atom, the effect of the other atoms in the scattering material being very small compared with this single large deflexion. In compound scattering, on the other hand, the final deflexion of the particle is the resultant of a very large number of small deflexions of the same order of magnitude. Both these types of scattering can be easily realized in the case of α-particles. The phenomena of single scattering are essentially simple, and it is easy to interpret the results of experiment in terms of the structure of the atom. Thus the observations, particularly of Geiger and Marsden †, and also of one of us ‡, have given the strongest possible support to the Rutherford conception of the atom and the theory of single scattering. It is not so simple to interpret quantitatively the experiments on compound scattering, and, speaking generally, the best that can be done is to show that the results are in accord with the theory of the nuclear atom. Such deductions have been drawn from measurements of the compound scattering of α-particles both by Geiger § and by Mayer ‖.

While the experiments on the scattering of α-particles are of a simple and straightforward character, the corresponding experiments with β-particles are attended by numerous difficulties, some of which arise from the nature of the available sources of β-particles, while others are due to the small energy of the particles. In contrast to the α-radiation the β-radiation emitted by a radioactive source is not homogeneous, but composed of particles of widely differing

* Communicated by the Authors.
† Geiger & Marsden, Phil. Mag. xxv. p. 604 (1913).
‡ Chadwick, Phil. Mag. xl. p. 734 (1920).
§ Geiger, Proc. Roy. Soc. A, lxxxvi. p. 235 (1912).
‖ Mayer, *Ann. d. Phys.* xli. p. 931 (1913).

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velocities. In order to work with a beam of β-particles of a suitably narrow range of velocity, it is necessary to sort them out in a magnetic field, with the result that the available primary beam of particles is of relatively small intensity. In most experiments, radium B + C has been used as the source of β-rays, and the strong γ-radiation emitted by this source adds a further complication to the experimental problem. The definiteness of the experiments on the scattering of α-particles is largely due to the simplicity and certainty of the scintillation method of counting the particles. For the β-rays no such method is available. Whatever means are used to detect the β-rays, the measurement of the scattered beam of β-rays, which must usually be of very small intensity, in the presence of a strong γ-radiation is a matter of some difficulty. Again, owing to the small energy of the average β-particle, the chance of scattering is so great that there may be some doubt as to whether, under the experimental conditions, the effects observed are to be ascribed to single or to compound scattering, or to an intermediate type.

For these and other reasons, the conclusions which have been derived from the measurements of the scattering of β-particles are not of that definite and clear-cut character shown by the corresponding experiments with α-particles, and, in fact, some observers have found it difficult to reconcile their results with the accepted views of atomic structure.

The early experiments of Crowther * were carried out before Rutherford put forward the theory of the nuclear atom, and were therefore interpreted in terms of the Thomson atom and on the assumption of compound scattering. It was shown later by Rutherford that the observations could also be approximately explained on the nuclear theory of the atom and on the hypothesis of single scattering.

Recently, experiments on the scattering of β-rays have been made by Geiger and Bothe †, by Crowther and Schonland ‡, and by Schonland §.

The experiments of Geiger and Bothe dealt mainly with compound scattering, and on the whole their results were in good accord with the corresponding experiments on α-rays. At the smallest thicknesses of scattering material the amount of scattering was decidedly less than that given by theory, indicating that the conditions for the application of the

* Crowther, Proc. Roy. Soc. A, lxxxiv. p. 226 (1910).
† Geiger & Bothe, *Zeit. f. Phys.* vi. p. 204 (1921).
‡ Crowther & Schonland, Proc. Roy. Soc. A, c. p. 526 (1922).
§ Schonland, Proc. Roy. Soc. A, ci. p. 299 (1922).

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theory of compound scattering were no longer fulfilled, and that single scattering began to be appreciable. They did not attempt to make observations of single scattering.

Crowther and Schonland carried out a detailed investigation of the scattering of β-rays under conditions in which they considered the theory of single scattering was applicable. Their results showed marked divergences from the Rutherford theory. The amount of scattering by light elements, such as carbon and aluminium, was several times that to be expected theoretically for all angles investigated (4° to 18°). On the other hand, for heavy elements such as gold and platinum, the scattering for small angles agreed fairly well with theory, but increased rapidly with the angle until for an angle of 18° it was in agreement with the scattering shown at all angles by the lighter elements. As a possible explanation of their results, Crowther and Schonland put forward a tentative suggestion that either the law of force close to the nucleus was not that of the inverse square, or that the electron might have a magnetic moment.

Later, Schonland repeated the experiments for larger angles of scattering, and obtained results in fair accord with theory. He endeavoured to explain the previous results by attributing the large scattering shown by the light elements to an effect of the divergence of the primary beam of β-rays, and by ascribing the deficient scattering at small angles by heavy elements to the screening of the nuclear charge by the K and L groups of electrons. His calculation of the influence of the divergence of the primary beam is certainly not correct, and, indeed, Jeans has shown that provided conditions for single scattering are fulfilled, the effect of a small divergence is negligible. Further, it appears to us that far too much weight has been given to the screening effect of the inner electrons in the case of the heavy atoms.

The explanation of the discrepancy between the results of Crowther and Schonland and the predictions of the theory of single scattering lies in the fact that their experiments are mainly concerned not with single scattering, as they supposed, but with compound scattering or with a type of scattering between the two. In their experiments they measured the thickness of material necessary to scatter one-half of the particles incident on it through more than a prescribed angle ϕ. Now, if the probability that a particle should be scattered through an angle ϕ is 1/2, then the probability that it should be scattered twice through this angle is 1/4. When we take into account the variation in the scattering with angle, it is clear that the particles scattered through more

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than ϕ must consist to a large extent of particles which have suffered more than one deflexion. This explanation of Crowther and Schonland's results has also been given by Bothe *, and he has shown that some of their results are in approximate agreement with those of Geiger and Bothe, and therefore with corresponding experiments on the scattering of α-rays. Detailed investigations, made by H. A. Wilson †, Jeans ‡, and Wentzel §, lead to the same conclusion. Jeans showed how difficult it is to disentangle the effect of single scattering from that of compound scattering when both are present, but was able to account in a general way for the results of Crowther and Schonland. Wentzel has developed in detail the theory of scattering for the transition type between the two extremes of simple and compound scattering—that is, for conditions in which the final deflexion of the particle is the result of a few single deflexions through angles of medium size. Scattering of this type may be termed, for want of a better word, "plural" scattering. He has shown that under certain conditions "plural" scattering may be more important than single scattering, or, in other words, that the deflexion of the particle through a certain angle is more likely to occur in a small number of medium steps than in a single large step. The scattering observed under these conditions will therefore be greater than that predicted by the theory of single scattering, in agreement with the observations of Crowther and Schonland. Wentzel has also obtained a criterion for the presence of single scattering. The argument by which he arrives at this is briefly as follows. A particle passing through the scattering foil is at every instant subjected to the influence of the external atomic fields. The very small deflexions of the particle due to these fields must be left out of account, for we are only concerned with the deflexions due to the internal fields of the atoms. As the external field merges continuously into the internal field it is somewhat arbitrary to fix any definite boundary to the atomic field, or a corresponding lower limit for the deflexion of the particle which may be considered in the calculation. For the present purpose, however, we may ascribe a definite radius R to the sphere of influence of the internal atomic field, and regard all particles which do not penetrate within this distance of the centre of an atom as undeflected. A particle which just penetrates into this region will undergo a

* Bothe, *Zeit. f. Phys.* xiii. p. 368 (1923).
† H. A. Wilson, Proc. Roy. Soc A, cii. p. 9 (1923).
‡ Jeans, Proc. Roy. Soc. A, cii. p. 437 (1923).
§ Wentzel, *Ann. d. Phys.* lxix. p. 335 (1922).

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deflexion ω. Limiting the action of the atomic field in the above way is then equivalent to neglecting all deflexions less than ω. In any investigation of the scattering of particles the conditions of experiment must be so adjusted that the total angle of scattering through which the particles are observed is several times greater than this minimum deflexion ω. Otherwise the possibility arises that the greater part of the particles have attained their final deflexion by a combination of several single deflexions each less than ω. We thus arrive at an upper limit to ω and a corresponding lower limit to R. This, then, gives a lower limit to the number of atomic encounters which the particle makes in passing through the foil. Only if this number is less than 1 can the type of scattering be considered as mainly single scattering. If the scattering foil is of thickness t and contains n atoms per c. c., then the average number of atoms traversed by the particle in passing through the foil is $\pi R^2 nt$. Wentzel shows that the most probable is equal to the whole number between $\pi R^2 nt$ and $\pi R^2 nt - 1$. If this is less than 1, then the scattering consists mainly of single scattering. The criterion for single scattering is thus

$$\pi R^2 nt < 2,$$

or R must not be greater than

$$R_{max.} = \sqrt{2/\pi nt}.$$

A particle which traverses an atom at this distance $R_{max.}$ from the nucleus will suffer a deflexion $\omega_{min.}$ Deflexions less than $\omega_{min.}$ must occur so seldom that they cannot contribute appreciably to the measured scattering. Wentzel then shows that repeated single deflexions through angles of less than $\omega_{min.}$ will not contribute markedly to the scattering, provided that the observed angle of scattering ϕ is at least a small multiple of $4\omega_{min.}$ This is then a sufficient criterion for the presence of single scattering under the given experimental conditions—viz., a thickness t of scattering foil containing n atoms per c. c., and an angle of scattering ϕ.

Applying this criterion to the experiments of Crowther and Schonland, Wentzel found that it was not fulfilled. By a detailed calculation of the effect of "plural" scattering he was able to account for their results on the basis of the accepted theory of atomic structure.

At the time the experiments which follow in this paper were begun, the above calculations of Wentzel had not been published. While we saw no reason to doubt the validity of the general theory of scattering and atomic structure, yet in view of the disagreement between the conclusions of different observers, it appeared to us advisable to conduct, in as simple

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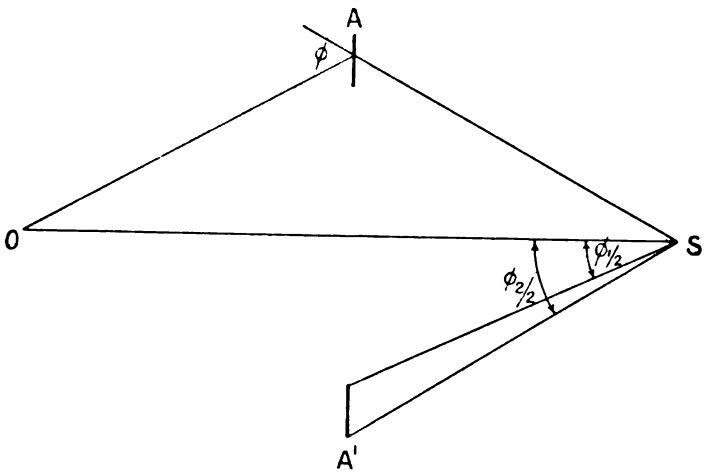
a way as possible, a few experimental tests in which the conditions for single scattering were at least approximately observed. These experiments will now be described.

§ 2. *The Method of Measurement.*

The method of studying the single scattering of β-rays was similar in principle to that used by one of us* in some measurements of the scattering of α-particles.

The particles from a source S (fig. 1) are scattered by a thin foil AA′, in the form of an annular ring, to a point O on the axis of the cone SAA′, such that OA = AS. It was shown in the previous paper that on the theory of single

Fig. 1.



scattering the number of particles scattered per second to unit area at O is

$$\frac{Qntb^2}{64r^2}\Big[\log\tan\phi_2/4 - \log\tan\phi_1/4 - \cot\phi_1/2\operatorname{cosec}\phi_1/2 - \cot\phi_2/2\operatorname{cosec}\phi_2/2\Big]$$

where $\phi_1/2$, $\phi_2/2$ are the angular limits of of the foil, and

Q = the number of particles emitted per second by the source,

t = thickness of scattering foil,

n = number of atoms per c.c. in the scattering material,

$b = Ne^2/T$, where N is the atomic number of the scattering atom and T is the initial kinetic energy of the particle.

* Chadwick, *loc. cit.*

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The number of particles falling directly on unit area at O is

$$\frac{Q}{4\pi l^2}, \qquad \text{where } l = OS.$$

By allowing the β-rays to enter an ionization chamber provided with a small opening at O we can thus measure in a simple way the fraction of β-particles scattered by a foil between two fixed angles.

This method of measuring the scattering of particles has several obvious advantages. For example, the ratio of the scattered beam of particles to the direct beam is so high that the thinnest sheets of foil can be used. Further, the area of the scattering foil is so large that the error due to lack of uniformity is rendered inappreciable.

Its application to β-ray scattering, however, is attended by one serious disadvantage. As is well known, the β-rays emitted by a radioactive body consist of particles of widely differing velocities, and in order to obtain a homogeneous pencil it is necessary to sort out the rays in a magnetic field. We found it very difficult to devise a suitable combination of the magnetic separation and the above method of observing the scattering, and preferred to use the heterogeneous β-rays emitted by a source of radium E as the primary pencil. This lack of homogeneity of the primary beam is of little moment in the comparison of the scattering by different elements, but becomes very important when we estimate the actual fraction of scattered particles, for the chance of scattering varies inversely as the square of the energy of the particle.

In the above calculation we have assumed that the mass of the β-particle remains constant in the orbit; that is, we have assumed that the increase in kinetic energy of the particle as it approaches the nucleus goes wholly in increasing its speed. Since the mass of the particle increases with the velocity, it will actually move more slowly in the nuclear field than in the case considered in the calculation, and its deflexion will be greater. The orbit of the β-particle when the variation of the mass with speed is taken into account has been calculated by Darwin *, and he has also worked out the correcting factor which must be applied to the simple theory. This correction depends on the angle of scattering and on the velocity of β-rays. It will be introduced when we calculate the fraction of particles scattered by aluminium (§ 6).

* Darwin, Phil. Mag. xxv. p. 201 (1913).

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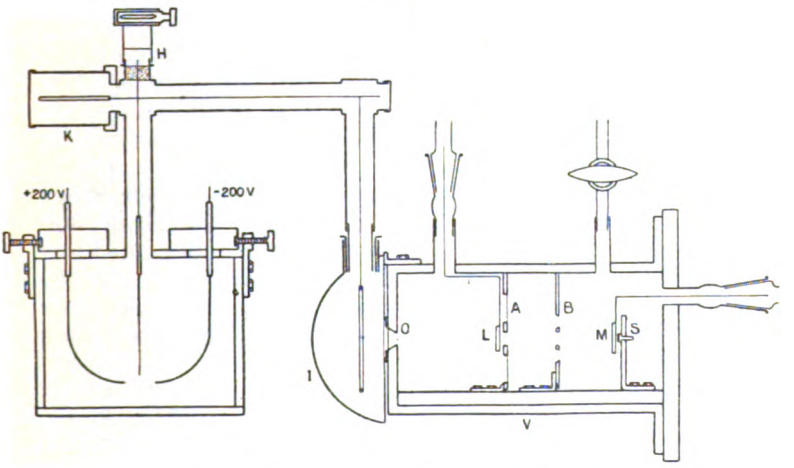
We have also neglected the effect of encounters of the β-particles with the electrons in the scattering material. On account of the small charge of the electron this effect is relatively small. It is easily seen that the electronic scattering can be included by putting the b in the above expression equal to $\sqrt{(N^2 + N)} \times e^2/T$. The contribution of the electrons to the scattering is thus only appreciable in the case of the lighter elements. For aluminium it is about 7 per cent. of the total scattering, for gold about 1 per cent.

3. *The Apparatus.*

The apparatus is shown diagramatically in fig. 2. The diaphragm B served to limit the beam of β-rays from the

Fig. 2.



source S, and consisted of a circular disk of 11·22 mm. diameter suspended in a circular opening of 19·30 mm. diameter. The scattering foil was held on the support A, equidistant from the source S and the opening O, through which the particles entered the measuring apparatus. The distance from the source to the diaphragm B was 26·5 mm. and from the source to the opening O, 100 mm. The source, diaphragm, and foil-holder were mounted on a brass base which fitted into slides in the brass box V, and were adjusted so that their common axis was central to the opening O. The diaphragm and foil-holder were made to fit closely to the sides of the box so as to prevent as far as possible the entrance through O of particles scattered by the walls of

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the box. The opening O, of 5 mm. diameter, was covered with a sheet of aluminium of just over 4 cm. stopping-power for α-rays, sufficient to cut out the α-particles from any polonium which might be present on the source.

The direct pencil of β-rays, which came through holes in the central disks of A and B, could be cut off at will by the movable lead screen L, and both direct and scattered pencils could be cut off by bringing the screen M in front of the source.

The brass box was evacuated by means of a Fleuss pump, and then by charcoal cooled in liquid air. It was found that the scattering of the rays by residual air in the box was negligible so long as the pressure was below ·5 mm., but the final experiments were all carried out in a charcoal vacuum.

The β-particles passing through the opening O were measured by the ionization they produced in the hemispherical chamber I. Thus the scattered particles and the direct particles had the same length of path in the chamber, and the ratio of the ionization currents gave the ratio of the numbers of particles in the scattered and direct beams. The ionization currents were measured by means of an electrometer of the type devised by Beatty *. This consists of a gold leaf hanging between two oppositely charged plates. The deflexion of the gold leaf was observed by a microscope of 85 × magnification. The sensitivity was about 300 divisions of the eyepiece scale per volt. A null method was used in which the current in I was compensated by the charge induced on the inner electrode of the small condenser K, the outer case being connected to a sliding contact on a potentiometer.

When no scattering foil was in position, a small current was obtained in I, due to the natural leak and to β-rays scattered from the walls of the box and edges of the diaphragms. This was balanced by a weak ionization produced in the small chamber H.

When measuring the scattered rays the condenser K was charged gradually to two volts, keeping the gold leaf as near as possible to its undeflected position. For measurement of the direct rays, the intensity of which was between 10 and 100 times that of the scattered rays, the potential was increased to ten volts. In some experiments the direct beam was reduced to about the same intensity as the scattered beam by rotating a wheel containing a suitable slit between the hole O and the ionization chamber. The two methods gave concordant results.

The source of β-rays was a disk of 3·8 mm. diameter coated with a deposit of radium E, obtained by electrolysis

* Beatty, Phil. Mag. xiv. p. 604 (1907).

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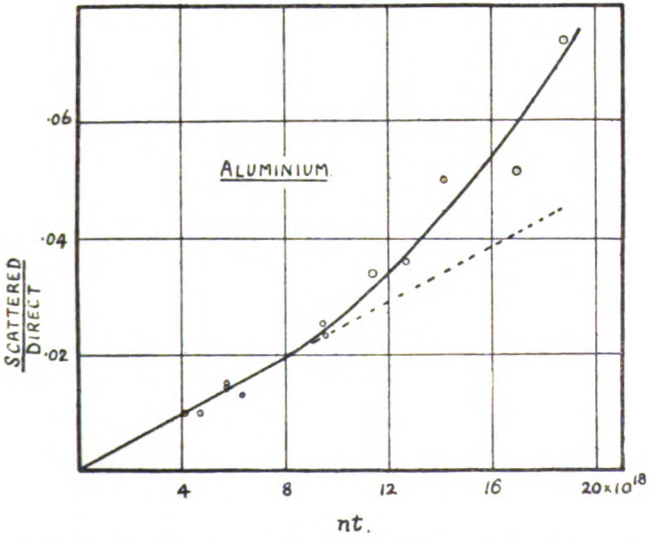
of a solution of radium D, E, and F. The purity of the radium E was examined by observing the rate of decay of activity of the source. In only one case was the source found to contain a detectable amount of radium D. The initial activity of the source was about equal to that of 1 mg. Ra (B + C) as compared on a β-ray spectroscope.

§ 4. *Test for Single Scattering.*

At the beginning of an experiment the lead screen L was rotated in the path of the direct rays. The small ionization current in I, due to the natural leak and to particles scattered from the walls of the box, was then balanced by means of the compensation chamber H. On moving L away, the direct beam entered I and was measured. The scattering foil, say one thickness of the thinnest aluminium leaf, was then placed on the support A, and the scattered beam was

Fig. 3.



measured with the screen L in position. Several measurements of the scattered beam alone and of the direct beam together with the scattered beam were made, and then the scattering foil was replaced by a foil of two thicknesses of aluminium, and the process repeated. The sensitivity of the electrometer could be checked at any time on rotating the screen M in front of the source, and so cutting off all β-particles from the ionization chamber.

In this way the results shown in fig. 3 were obtained for

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aluminium as scattering material. The ordinates represent the ratio of the scattered rays to the direct rays, and the abscissæ the value of nt for the foil used.

If the conditions for single scattering are fulfilled, the curve obtained should be a straight line passing through the origin. It is seen that this is true only for small values of nt. For larger values the experimental curve is much higher than the straight line passing through the earlier points, indicating that with these thicknesses multiple scattering begins to play an appreciable part. The thinnest foil of aluminium we could obtain had a weight of ·184 mg./sq. cm., corresponding to a thickness of ·68 μ and a value of nt of $4{\cdot}1 \times 10^{18}$. The results show that even with only four thicknesses of this foil the scattering is not entirely single scattering. These measurements bring out very clearly the difficulty of obtaining conditions under which true single scattering of β-particles takes place, but show at the same time that these conditions are realized in our experiments so long as we use the thinnest scattering foils.

We may here apply Wentzel's criterion for the presence of single scattering which we discussed in § 1—viz., that the angle of scattering ϕ should be a multiple of $4\omega_{\text{min.}}$, where $\omega_{\text{min.}}$ is the deflexion suffered by a particle which passes the scattering nucleus at a distance $R_{\text{max.}} = \sqrt{2/\pi nt}$. In these experiments, the minimum angle of scattering of the particles which were observed in the ionization chamber was 24°. For the thinnest sheets of scattering foil of the different elements examined, the values of $4\omega_{\text{min.}}$ varied from 2° 48′ to 5°. Thus Wentzel's criterion is fulfilled in all cases.

§ 5. *Comparison of Different Scattering Materials.*

Measurements were made of the scattering by four different materials—aluminium, copper, silver, and gold. The results are shown in fig. 4. As in fig. 3, the ordinates give the observed ratio of the ionization due to the scattered rays to that of the direct rays, while the abscissæ give the values of nt for the various scattering foils. In order to obtain all the curves satisfactorily on the same diagram, two scales of nt are used, one for aluminium and copper, and one for silver and gold, as shown in the figure.

It will be seen that for small values of nt the curve for each element is a straight line. This straight line, shown dotted in the diagram, is taken to represent the effect of pure single scattering. Copper and silver behave similarly to aluminium in showing for the thicker foils an excess scattering

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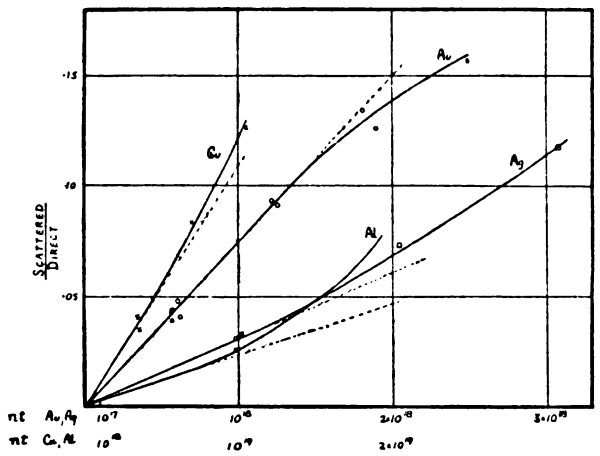
due to the appearance of multiple scattering. The curve for gold, on the other hand, is straight for some distance, and then falls slightly below the single scattering value. No weight is attached to this point, as only one observation was made with the greatest thickness of foil; but it is easy to see that multiple scattering should be less noticeable in the case of gold on account of the screening effect of the electrons in the inner orbits, corresponding to a smaller effective nuclear charge. This would make scattering through small angles less probable than we should expect from measurements at larger angles.

Fig. 4.



From these curves the single scattering by the four elements examined can be compared as in the following table, where the ratio of the scattered rays to the direct rays, for a foil for which $nt = 10^{18}$, is given in the second column for the element in the first. Before we compare these ratios, we must apply a correction for the scattering by the electrons in the material. As pointed out in § 2, the electronic scattering is 1/N times the nuclear scattering, where N is the atomic number of the element. In this way the corrected ratios of column 3, representing the nuclear scattering, are obtained, the ratio for aluminium being put equal to unity. On the theory of single scattering the ratio for a given element should be proportional to the square of the nuclear charge. Column 4 gives the ratios of the squares of the nuclear charges of Cu, Ag, and Au to that for Al, and comparison of columns 3 and 4 shows that the theory is verified within

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the accuracy of experiment in the cases of copper and silver. The discrepancy in the case of gold is explained by a calculation of the orbit of a β-particle scattered by a gold nucleus under the conditions of our experiments, when it appears that the path of the particle lies wholly outside the K-ring of the atom. Thus the effective nuclear charge of gold will be about two units less than the actual charge. On taking this into account, we get a close agreement between experiment and theory in the case of gold as well as with the other elements.

TABLE I.

Element.	$\frac{\text{Scattered}}{\text{Direct}}$ for $nt=10^{18}$.	Corrected.	N^2/N^2_{Al}.
Aluminium	·00234	1	1
Copper	·0113	5·03	4·98
Silver.....	·0302	13·5	13·1
Gold	·075	34·1	37·0

§ 6. *The Amount of Scattering.*

The next test we can apply is to compare the actual amount of the scattering observed experimentally with that to be expected on the theory. This is perhaps best done by using the theory to calculate from the observations the nuclear charge of the scattering elements. This calculation need be performed only for one element, for we have shown in the previous section that the scattering varies for the different elements in the way demanded by theory.

We may write the fraction ρ of β-particles of kinetic energy T which are scattered through a given angle by an element of atomic number N in the form

$$\rho = K \,.\, b^2 \,.\, f^2(\phi, \beta),$$

where K is a constant involving the geometrical conditions of the experiment, $b = Ne^2/T$, and $f^2(\phi, \beta)$ * is the correction for the change of mass of the particle in its orbit round the scattering nucleus.

In the first place we notice that the chance of scattering is proportional to $1/T^2$, where T is the kinetic energy of the particle. Now the β-rays of radium E, the source used in our experiments, are not homogeneous, but differ rather widely in velocity, so that the estimation of the average value of $1/T^2$ is a somewhat unsatisfactory process. Mr. Madgwick, of this laboratory, has kindly investigated the

* *Cf.* Crowther & Schonland, and Schonland, *loc. cit.*

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distribution of the β-rays in the magnetic spectrum of radium E, measuring the intensity of the rays for different values of $H\rho$ by an ionization method. The curve showing the intensity of the rays against the value of $H\rho$ is similar to a probability curve, and has a pronounced maximum at 2200 $H\rho$. From his results we find an average value of e^2/T^2 of $2{\cdot}25 \times 10^{-6}$ e.s. units. This corresponds to an energy of 200,000 volts and a velocity of ·70 c. We are also indebted to Dr. Bothe, of the Reichsanstalt, Charlottenburg, for information on this question. Dr. Bothe measured the intensity of the rays of different energies by a photographic method, and, taking into account the different conditions of absorption, his results agree very closely with those of Mr. Madgwick.

In the next place we have to calculate the average value of the relativity correction, $f^2(\phi, \beta)$, for the conditions of our experiments. For a particle of velocity βc scattered through an angle ϕ this correction is

$$f^2(\phi, \beta) = \frac{\operatorname{cosec}^2\psi}{\left\{\dfrac{\beta \,.\, \cot \phi/2}{2(1-\sqrt{[1-\beta^2]})}\right\}^2},$$

where $$\beta \cot \psi = \tan\{\pi - (\cos\psi)\tfrac{1}{2}(\phi+\pi)\}.$$

In our experiments the scattering angle varied from 20° to 40°, but fortunately the correction changes fairly slowly with the angle. The average value was found to be 1·80.

The expression for K has been given in § 2. Putting in the values of $\phi_1/2$ and $\phi_2/2$, 11° 58′ and 20° 1′ respectively, and taking a scattering foil for which the value of nt is 10^{18}, we find

$$K = 1{\cdot}11 \times 10^{19}.$$

Finally, we have for the fraction of particles scattered under the prescribed conditions by a nucleus of charge N,

$$\rho = 1{\cdot}11 \times 10^{19} \times (Ne)^2 \times 2{\cdot}25 \times 10^{-6} \times 1{\cdot}80$$
$$= (Ne)^2 \times 4{\cdot}5 \times 10^{13}.$$

To take the electronic scattering into account, we must write (N^2+N) for N^2 (§ 2), and we get

$$\rho = (N^2+N)e^2 \times 4{\cdot}5 \times 10^{13}.$$

This represents the total scattering under our conditions by a sheet of matter of nuclear charge Ne of thickness corresponding to a value of $nt = 10^{18}$.

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We found (§ 5) that the observed fraction of rays scattered by aluminium was equal to ·00234.

The atomic number of aluminium is therefore given by

$$\cdot 00234 = (N^2 + N)e^2 \times 4\cdot 5 \times 10^{13},$$

whence

$$N = 14\cdot 6$$

instead of 13, the true atomic number. The scattering observed is thus greater than that calculated in the above way, and this is the case for all four elements investigated.

§ 7. *Discussion of Results.*

In the previous sections we have shown that it is possible to obtain conditions of experiment in which the single scattering of β-particles can be observed, and we have compared the results of such experiments with the theory of single scattering.

In the first place, it has been shown by comparing the amount of scattering by four elements, viz. aluminium, copper, silver, and gold, that the nuclear scattering is proportional to the square of the atomic number of the element. In this comparison the small amount of scattering due to the electrons in the atom was deducted.

Secondly, the value of the nuclear charge of aluminium has been calculated from the scattering measurements to be 14·6 units, instead of the true value of 13 units, indicating that the scattering is a little greater than that to be expected on the theory. In considering this point, however, we must remember that the β-particles used in the experiments were heterogeneous, and that consequently an average value of $1/T^2$ had to be calculated from measurements of the magnetic spectrum of the particles. This calculation cannot be made with any great accuracy. Further, we have compared the numbers of β-particles in the scattered and direct beams by comparing the ionizations produced by them. This will only be correct when the average particle in each beam has the same ionizing power. This is not the case, for, since the scattering is inversely proportional to the square of the energy of the particle, the scattered beam of β-rays is on the average of lower velocity than the direct beam, and will therefore produce more ionization per particle. On the other hand, the scattered beam will suffer a greater absorption in the aluminium window at O, not only on account of the lower velocity of the rays, but also on account of the obliquity of the beam.

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An attempt was made to take these factors into account in the following way. The absorption coefficients of the scattered and direct beams were measured, using an absorbing foil of aluminium of the same thickness as that over the window O. They were found to be 144 cm.$^{-1}$ and 58 cm.$^{-1}$ respectively. It follows at once that to allow for the increased absorption of the scattered beam we must multiply the observed ratio of scattered to direct ionizations by the factor 1·29. In order to determine the correction for the greater efficiency of the scattered particles in the ionization chamber, we need to know how the ionizing power of a β-particle changes with the absorption coefficient. We may assume with Rutherford * that, to a fair approximation, the absorption coefficient of the β-particle is proportional to $T^{-3/2}$, where T is the energy of the particle, and that its ionizing power is proportional to $T^{-1/2}$. The ionizing power is thus proportional to the cube root of the absorption coefficient. In our experiments, therefore, the scattered particle had an ionizing power 1·36 times that of the direct particle, and we must reduce the observed ratio of scattered to direct ionizations by this factor in order to get the ratio of particles in the two beams. Thus the final correcting factor is 1·29/1·36 = ·95. These corrections thus reduce our experimental value for the nuclear charge and bring it nearer to the true value.

Taking the above considerations into account, we conclude that the agreement between theory and experiment is as satisfactory as one could expect. We may at least say that there is no marked discrepancy between theory and experiment. It is, of course, possible that the excess scattering observed may be due to a loss of energy by radiation as the β-particle describes its orbit in the nuclear field. To investigate this question it would be necessary to use a primary pencil of homogeneous β-rays, and for such work our experimental arrangement is not suitable.

There is one further point on which some remarks may be made. In their paper, Crowther and Schonland mentioned that their results were rendered less regular by the introduction of the relativity correction term, $f^2(\phi, \beta)$, and later H. A. Wilson † and Davisson ‡ have suggested that Darwin's method of calculating this correction should be modified.

* Rutherford, 'Radioactive Substances,' p. 238 *et seq.*
† H. A. Wilson, Proc. Roy. Soc. A, cii. p. 9 (1923).
‡ Davisson, Phys. Rev. xxi. p. 637 (1923).

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In the first place, it should be pointed out that Crowther and Schonland applied far too large a correction term to their results, because they assumed that they were dealing with single scattering ; that is, they put ϕ equal to the total angle of scattering. Actually, their particles were deflected several times in undergoing the total deflexion, and for such small angles the relativity correction is barely appreciable. In the second place it must be remembered that the explanation of the fine structure of the lines of hydrogen and ionized helium depends on an exactly similar application of a relativity correction, and that this has been beautifully confirmed by Paschen's measurements. We have therefore no reason to doubt the validity of Darwin's calculation.

§ 8. *Summary.*

In this paper we have described some experiments on the scattering of β-rays, in which the conditions for single scattering were approximately fulfilled. The scattering angle was between 20° and 40°, and the thinnest obtainable foils of matter were used.

The scattering by four elements, viz. aluminium, copper, silver, and gold, has been compared, and found to vary with the atomic number in the way demanded by the theory of single scattering.

The fraction of particles scattered under definite conditions has been measured. It appears that this fraction is slightly greater than is to be anticipated on the theory. Owing to the use of a heterogeneous beam of β-rays it was not possible to decide whether this discrepancy is genuine, or due to error in estimating the quantities concerned in the calculation of the theoretical fraction.

Our best thanks are due to Sir Ernest Rutherford for his interest in these experiments, and for placing at our disposal the necessary radioactive material.

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XXIV. *On the Electrification of Gases by Surface Combustion.* By J. DICKINSON, *M.A., M.Eng., Lecturer in Electrical Engineering in Armstrong College, Newcastle-upon-Tyne* *.

1. THIS work was suggested as a possible means of explaining certain phenomena of boilers and boiler furnaces now known to be associated with surface combustion—*e.g.*, the secondary effects accelerating corrosion, and the exceedingly high local temperatures reached.

There is also the question of wider theoretical interest, as to how far the electrical processes, which are now admitted to accompany all forms of chemical activity, can be identified in surface combustion. The study of electrification of gases under the influence of external sources of ionization has been so well worked out that the electrical phenomena of gaseous combustion should be capable of explanation in terms of accepted experimental evidence.

The experiments described have for their object the measurement of the rate of growth of charge gained both by a chamber in which surface combustion is taking place, and by an electrode surrounding the products of combustion after they have passed from this chamber. A measure of the ionization accompanying gaseous combustion of any kind is thus obtained.

The conductivity of the gases in intimate contact with the surfaces upon which the combustion is being accelerated has been examined in the present case, with a view to determining the dependence of the thermionic currents from the heated solid on various percentages of gas and air in the neighbourhood of the mixture which gives, theoretically, complete combustion.

If the extraordinary efficiency of surface combustion is due to the greater ease and completeness with which the gases are prepared for combustion by an intense electrical discharge from the hot surfaces, of the kind investigated by Richardson and Harker, it follows that, by varying the conditions under which surface combustion occurs, there should be a corresponding variation in the electrical phenomena observed, and that it should be possible to identify the state of perfect surface combustion by the electrical equilibrium of the gaseous products.

The phenomena most closely associated with the present investigation are those of the electrification produced by flame, which have been known for 150 years. The most

* Communicated by Prof. W. M. Thornton, O.B.E., D.Sc.

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characteristic fact of the electrification of flame is that there are two kinds of ions present. The unburnt gas carries a negative charge, while the burnt or burning gas carries a positive charge (J. J Thomson, 'Conduction of Electricity through Gases,' chapter ix.). It would appear from this, but it has never been previously investigated, that when the mixture is in the proportion for perfect combustion, and when the volume of flame or combustion is confined to a surface layer, so that there is no opportunity for variation of mixture during combustion, there should be no electrification produced. This is now found to be the case.

2. It is well known that solid surfaces provide a suitable field for the modification of mutual gaseous actions in many, if not in all cases, considerably accelerating many gaseous reactions. This attribute of extended solid surfaces is an essential in, and leads to the definition of, surface combustion. Thus surface combustion consists in utilizing the accelerating effect which hot surfaces exert on gaseous combustion (C. D. McCourt, 'Electrician,' lxxi. May 2nd, 1913). In the light of modern work on the electrification of gas near hot bodies, this acceleration can be regarded as activation or ionization of one or of both of the combining gases by the ionic discharge from the hot surface.

The leading principle of the Bonecourt process of surface combustion (*loc. cit.*) is the passage of a mixture of gas and air, adjusted to give complete combustion, through or over porous refractory materials. The theoretical proportions for complete combustion are 16 parts of gas to 84 parts of air by volume. When the refractory material has reached a certain temperature, the combustion takes place on the porous surfaces, all flame disappears, and the resulting radiant heat further increases the temperature of the surface on which it falls.

A tube packed with refractory masses of about one inch in diameter, through which the explosive mixture is drawn, is the method adopted in the following work. In this case the velocity of the mixture at inlet must be greater than the speed of ignition, which for the mixture theoretically giving complete combustion is greater than 16 feet per second. The fragments of refractory material then quickly become incandescent, accelerating combustion and producing high temperature. With a small percentage of air or of gas the mixture is non-explosive. Until the percentage of gas reaches about 16 the speed of ignition increases, the combustion accelerates, and the temperature rises with increased

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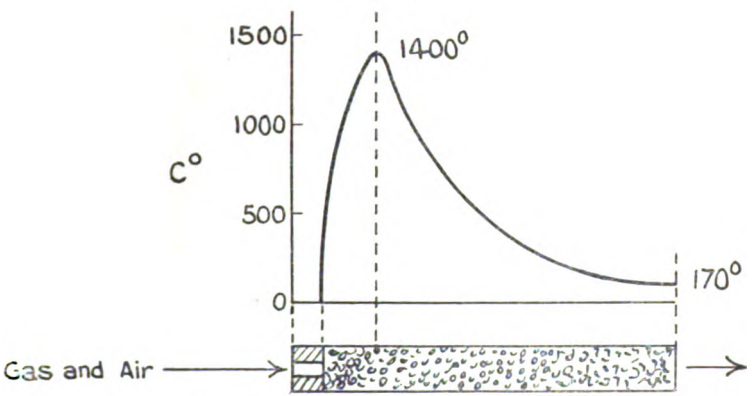
gas, keeping the air constant; but beyond this value for the gas there is deceleration both of combustion and of speed of ignition with consequent falling of temperature.

Fig. 1 shows a boiler tube, as used in this research, filled with refractory granules, on whose surface the combustion takes place. At the inlet the tube is fitted with a fire-clay plug having a central opening to admit the explosive mixture. The fragments of ganister or fire-brick touch the plug. After previous heating with flame, the gas is turned off and on again immediately, when it burns within the tube. Incandescence is quickly reached and combustion is complete within the first few inches of the tube, giving rise to a very steep temperature gradient throughout, as

Fig. 1.



shown in the diagram. The granules are also instrumental in withdrawing the heat from the hot gases, which leave the tube, when mounted in a boiler, at approximately 170° C. The difference of pressure between the entrance to the tube and the exit may be produced by direct pressure of about 1 lb. per square inch, or by suction. In the latter case, for a given adjustment of the suction mechanism, the quantity of air drawn through is constant, giving complete regulation by means of the gas cock, and inspection of the glow within the tube gives the correct adjustment. In consequence of this greatly increased heat of combustion at the critical value of the mixture which yields complete combustion, the present work has been undertaken to determine whether there is intense electrical activity which can be identified, and even whether there are currents in the metal tube which help the heat of combustion.

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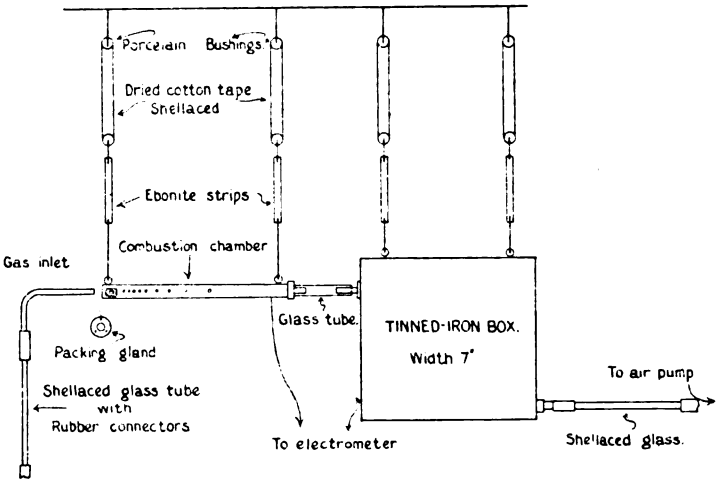
3. The apparatus consists of a 2-in. wrought-iron steam tube, packed with fire-brick granules of about 1 in. in diam., on the surface of which combustion is developed, and of a tinned-iron box into which the total products of combustion are drawn by a rotary suction pump, belt-connected and well earthed. The combustion chamber and box are suspended by means of ebonite strips and cotton tape impregnated with shellac, joined together by copper wire and porcelain bushings, and an air-tight joint of $1\frac{1}{2}$ in. glass tube connects them. The glass tube fits closely over asbestos-lagged adaptors.

Fig. 2.



Apparatus used.

Diagonally opposite to the inlet of the box is the outlet, by way of a 1-in. tube to the suction-pump. A glass insulating tube covered within and without with shellac connects the box to the pump through 1-in. rubber tubing. This arrangement gives the best possible circulation within the box, and affords the products of combustion opportunity of coming into contact with the walls of the vessel to impart to it any free charge they may be carrying. Thus both the combustion chamber and the box, or metal electrode, surrounding the products of combustion, are insulated from earth and from each other. The gas is controlled by a cock, and measured by a Griffin meter of the water type, calibrated to read 1/1200 cubic foot, and the jet is insulated as shown in the diagram (fig. 2).

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A Negretti & Zambra anemometer, reading to 5000 feet per minute, connected to the inlet by an air-tight paper cone, gave the number of feet of air passing per minute for those speeds at which the pump was driven. This was checked several times, giving only negligible differences in readings. From these results, by measuring the net area of the orifice at the anemometer, the volume of air passing per minute was calculated.

When the gas was turned on, the total volume of gas and air entering the combustion chamber was assumed to be that corresponding to the calibrated speed of the pump. In this way the gas percentage was derived by volume.

The combustion chamber has a small mica window a few inches from the inlet, enabling inspection of the interior to observe the maximum glow corresponding to perfect surface combustion. There are also a number of equispaced ¼-in. holes, bushed with clay-pipe stems, along the side of the combustion chamber, through which platinum electrodes may be inserted for examination of the electrification in intimate contact with the refractory surfaces. These tubules are sealed with fire-clay. A packing gland closes the entrance to the tube except for a central aperture 1-in. in diameter. This consists of an outer ring of diameter greater than that of the combustion chamber, and a stout iron ring which will move freely within the chamber. The equidistant set-screws serve both to hold the asbestos packing in position, and to swell out the asbestos packing when placed in the chamber and screwed up. The function of the central aperture is to increase the velocity of the mixture entering the chamber to a value greater than the speed of ignition in open tubes, otherwise combustion solely in the the chamber is impossible.

Electrometer Connexions.

The C. T. R. Wilson tilted gold-leaf electrometer used is shown diagrammatically (fig. 3), and was constructed, with slight modifications, according to the specifications in the Proc. Camb. Phil. Soc. xii. p. 135 (1903), and of Dr. G. W. C. Kaye in the Proc. Phys. Soc. 1901 and 'Electrician,' March 24, 1911.

It was found that ability to adjust the plate was advantageous, consequently the sulphur insulating the plate was moulded in an ebonite sleeve, which could be moved inwards or outwards. The make-and-break cup contained a strong

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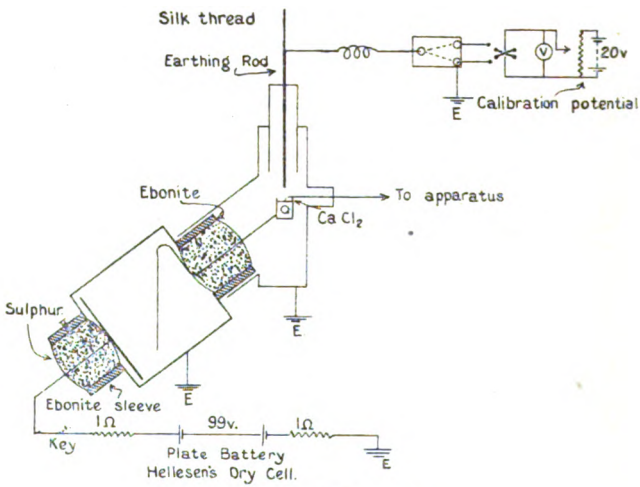
solution of calcium chloride, since mercury produced appreciable electrification by "splashing." A Reichert Wien micro-eyepiece and Number (1 *a*) objective, with requisite adjustments, enabled the leaf to be followed and focussed. The maximum sensitivity used gave a deflexion of 200 eyepiece divisions per volt over the working range. The plate was connected to the positive pole of a dry battery of approximately 100 volts, well insulated on a slab of paraffin wax 3-in. thick. It was found that the leaf returned to its zero position correctly, on earthing, after each set of readings

Fig. 3.



Electrometer and Connexions.

taken, showing that the high-tension battery was adequately insulated, since this controls the zero position of the leaf. The light illuminating the eyepiece scale was more than ten feet away from the electrometer.

The earths were all combined in one node and joined to a water main.

An earthed wire gauze of less than $\frac{1}{2}$-in. mesh completely enveloped the combustion chamber and box, and a lead-covered lead with sheath earthed, having sulphur bushings at each end, was used to connect the apparatus to the electrometer.

After many modifications of the system of insulation and protection, this final method ensured that the whole apparatus would retain a charge giving full-scale deflexion on the

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electrometer for sixteen hours with only the loss corresponding to less than five small-scale divisions, and that disturbances due to induction would be deleted.

The above precautions have been taken in order to eliminate the effects of capacity of the surrounding walls and bodies, and of local fields; otherwise, when working with such a sensitive instrument, the results are affected and are entirely spurious. To effect complete insulation of the whole apparatus was a difficult and lengthy operation, but without such insulation it was not possible faithfully to repeat the results.

Experimental Details.

The readings given by the gold-leaf electrometer are interpreted in terms of volts by means of calibration curves taken at the end of each series of experiments, and the points thus obtained are directly assembled in the figures shown. The points, therefore, are not the means of a number of determinations, but give the observed values in any particular case. Each particular case has been many times repeated, and the subsequent determinations have been correct within five per cent. The variations in the state of the combustible mixture and the temperature of air and objects surrounding the combustion chamber do not admit of closer approximation. The derived curves also are constructed from observed values in each particular case.

4. The first series of experiments is described to identify the sign of the electrification produced by surface combustion as distinct from that produced by flame.

Evidence of the sign of the the charge acquired by the tinned-iron box surrounding the products of combustion was obtained directly, by means of the gold-leaf electrometer, for various percentages of gas. The results, when the deflexions of the gold-leaf are interpreted in terms of volts, form a family of curves having the characteristics shown in fig. 4.

Fig. 4 shows the effect obtained under steady temperature conditions.

The curve is divided into two parts to illustrate the electrical effect of :—

(*a*) Surface Combustion—OF on curve.
(*b*) Flame—FH on curve.

In the latter case the gas is lit back to the feed-pipe by a wax taper.

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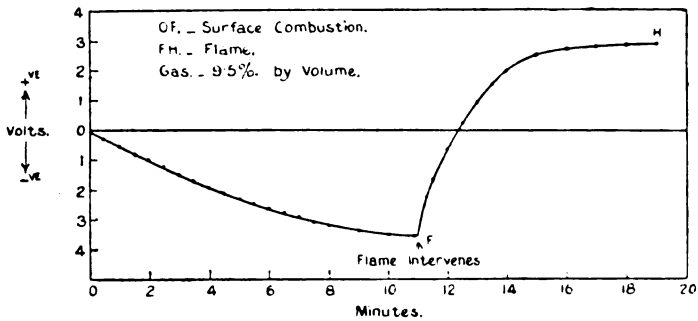
In the first part (OF) the gold leaf of the electrometer moves towards the positively-charged plate, showing that the sign of the electrification produced in the flue gases by surface combustion alone is negative. Thus there are negative ions present in the products of surface combustion with air in excess.

Fig. 4.



Electrification of the Tinned-iron Box.

The second part of the curve, or the portion onwards from the point F, illustrates the electrical condition of the flue gases after the intervention of flame. There is an immediate change of sign, and the direction of the deflexion shows, in accordance with modern experiment, a surplus of positively-charged ions.

This is a striking illustration of the opposite effects produced in the flue gases by surface combustion on the one hand and by flame on the other.

In fig. 5 the signs of the charges acquired by the *combustion chamber itself* in the two cases, for surface combustion and flame, are compared for the same gas percentage as in fig. 4.

During surface combustion the charge is wholly positive, while in the case of flame there is a short period when the charge is negative before changing to positive permanently.

The chamber is heated more slowly in the case of flame, but a larger amount of the tube forming the chamber is heated to redness than in the case of surface combustion. In surface combustion, however, the heat is much more intense and more localized towards the inlet.

In the curve representing the effects due to surface combustion the chamber is clearly positive, emitting electrons profusely when steady conditions producing bright redness have been reached. The well-known positive

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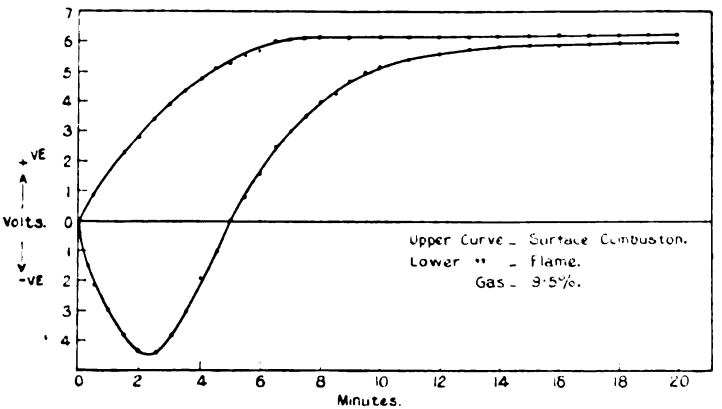
emission from the tube at low temperatures probably accounts for the departure of the initial portion from a straight line. On the other hand, the charging up of the chamber gives rise to a back E.M.F. which tends to stop the current. A limiting potential is reached which is sufficient to arrest further action. This is shown by the curve reaching a steady or saturation value in each case.

The negative portion of the flame curve shows the conditions within the combustion chamber prior to the activation by discharge of negative ions from the refractory fragments, and not until a certain temperature is reached, shown by the minimum point on the curve, is this activation by negative discharge from the refractory masses possible.

Fig. 5.



Combustion Chamber.

Thus, comparing the effects displayed by the combustion chamber and the tinned-iron box, the electrification produced by surface combustion is positive in the former and negative in the latter, showing that the ionic or electronic attack upon the combustible is vigorous, surplus negative ions being carried over in the gaseous products to the tinned-iron box. However, in the case of flame, the available electrons are insufficient for the combining gases, and excess positive ions are carried over in the products of combustion. The result of this scarcity of activation is slower combination of the gases forming the combustible, and consequently less intense radiation, although the total heated surface within the combustion chamber is appreciably greater than that during surface combustion, as shown by the region of redness of the tube.

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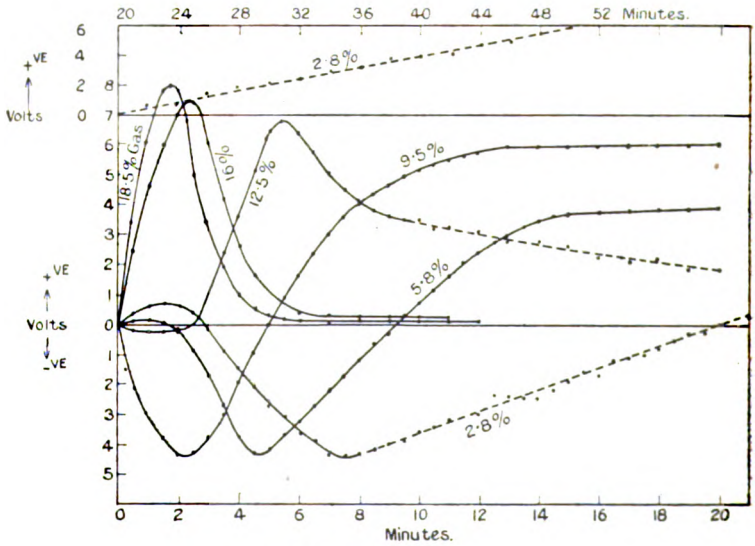
5. Examination of the electrical conditions in the combustion chamber and in the products of combustion for various mixtures, with a view to identifying perfect combustion by electrical means.

Fig. 6 is a family of curves showing the growth and decay of charge acquired by the combustion chamber with combustible of various percentages, including and exceeding that percentage which gives, theoretically, perfect combustion. The combustion here is by flame alone, and each curve is taken with the combustion chamber cold at the start.

Fig. 6.



Combustion Chamber—Flame.

Beginning with the least percentage of gas, the first portion is positive, such as would be produced by positive ions crossing from the hot granular packing, as one electrode, to the cold tube as the other. The effect is transitory, and depends for its detection on the rate of heating of the tube. The slower the tube is heated, the more readily is this observed. It is possibly an example of the Thomson effect for a vapour, as suggested by Harker under similar conditions *in vacuo* (Proc. Roy. Soc. Ser. A, April 25, 1912). The second and third portions of this curve are analogous to the third curve, which is the lower curve of fig. 5.

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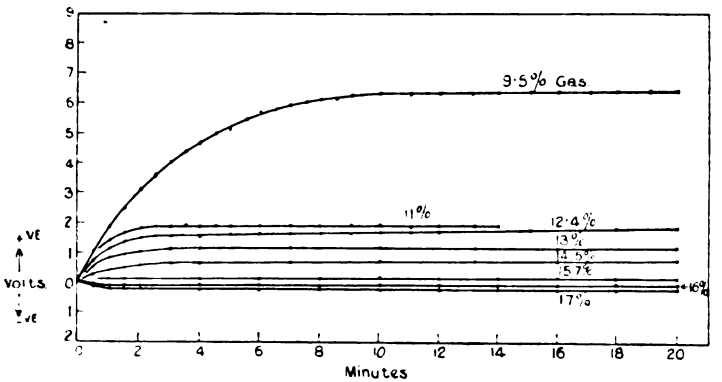
With larger percentages of gas, the negative portion decreases rapidly, the rate of charging, positively, increases, and the heat of the tube becomes more intense, producing an increasingly profuse negative emission from the granules, which reduces the positive charge on the tube, but does not entirely neutralize it. This emission, increasing with temperature, accelerates the combination of the gases, but does not reach a sufficiently high value to effect a change of sign. Further attempts to increase the gas percentage resulted in a violent explosion in the tinned-iron box.

Fig. 7 is a similar family of curves showing the effects of percentage mixture upon the charge acquired by

Fig. 7.



Combustion Chamber—Surface Combustion.

the combustion chamber when surface combustion is being developed within it, for percentages of 9·5 and above. The curves for percentages below this value occurred in the reverse order, but were of the same sign, and, being similar, are omitted for clearness.

The electrification is positive, and decreases rapidly for percentages between 12 per cent. and 16 per cent. At 15·8 per cent. there is no evidence of electrification on the combustion chamber, but for values above 15·8 per cent. the sign of the charge produced by the products of combustion is changed. This suggests that it might conceivably be possible to determine when perfect combustion is obtained in a boiler furnace by sampling the flue gases and testing the sign of their electrification.

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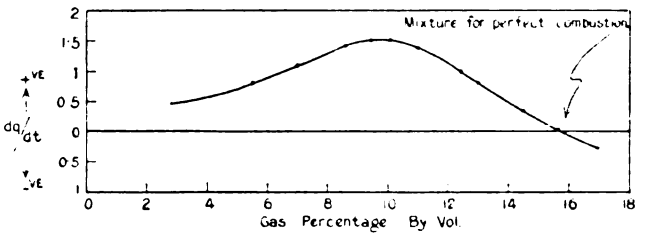
Rates of Growth of Charge.

6. Fig. 8 is a derived curve for the combustion chamber. Since the capacity of the system has been maintained constant, the rate of change of volts will give a measure of the growth of charge. Consequently for this curve the rate of increase of volts during the early stages of the curves in fig. 7 is a measure of dq/dt or the conduction current produced by the passage of electrons or ions. This "Conduction Current" is plotted against per cent. of gas, and is a maximum for a combustible mixture of 9·5 per cent. gas. The curves for percentages less than 9·5 per

Fig. 8.



Combustion Chamber—Surface Combustion.

cent. have the same form as those above 9·5 per cent. These latter are assembled in fig. 7.

It was not possible to maintain surface combustion below 2·5 per cent., the cooling effect of the air-stream upon the granules being too great.

From this curve it appears that the number of negative ions discharged into the combustible mixture by the red-hot material increases up to 9·5 per cent. of gas, and then falls, until at 15·8 per cent. the electrical discharge is zero. This means that, when the mixture is reached in which inflammable gas and air are in the proportions for perfect combustion, the electrification given out by the red-hot material is completely utilized in the activation of the combining gases. At this point, as will be seen in the next figure, 9, there is no electrification of the products of combustion. Figs. 8 and 9 show conclusively that perfect surface combustion is a state of electrical equilibrium, all the surplus electrical discharge being completely taken up by the gases in the combustion chamber, so that there are no ions in the products of combustion.

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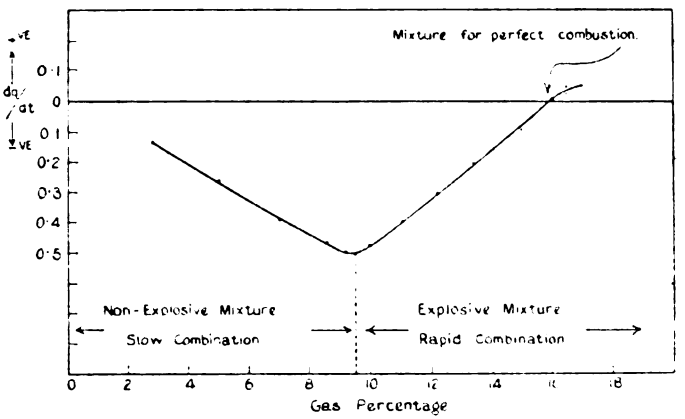
The function of the heated granules is seen to be the production of electrons or ions in increasing numbers until the percentage of 15·8 per cent. is reached, when the combustion is perfect and the activation of the combining gases is the greatest possible. At this point, the point of perfect surface combustion, the electrical system seems totally self-contained, and neither the combustion chamber nor the tinned-iron box surrounding the products of combustion gives evidence of the slightest electrification. This outstanding phenomenon is also shown in the next figure.

Fig. 9.—The tinned-iron box, when surface combustion is taking place in the combustion chamber, receives negative charge at an increasing rate for percentages up to 9·5 per cent., and then the rate decreases until at 15·8 per cent.,

Fig. 9.



Tinned-iron Box—Surface Combustion.

approximately, there is no evidence of electrification. This process is the reverse of that occurring in the combustion chamber, as might be expected, and shows that electrons or negatively charged ions are swept over into the flue gases. The capacity of the combustion chamber is less than that of the tinned-iron box, and this is shown in the different charging rates.

The straight-line slopes of the curves of figs. 8 and 9 are similar to those of the velocities of explosion waves in open tubes *.

* R. V. Wheeler, Journ. Chem. Soc. Trans. p. 2608 (1914).

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Below 9·5 per cent. the lower limit of inflammability, the mixture cannot support self-ignition, or, in other words, is non-explosive. This is an indication of rapidity of combination, for the difference between mixtures just below and just above the lower limit is entirely one of rapidity of combination. The more rapid the combination the greater the drain or utilization of the electrification supplied by the hot material.

Examination of Modifying Causes.

7 (*a*). In order to eliminate the effects arising from suspected ionic currents within the combustion chamber, which may help the heat of combustion, a series of experiments was undertaken.

Platinum exploring wires 2 mm. apart were inserted to a depth of 3 cm. along the tube forming the combustion chamber, and a reversible potential of 2 volts was impressed upon them. The low voltage was used in order that ionization by collision in the gases might be negligible. A sensitive tangent galvanometer detected the currents.

The maximum current for surface combustion at 9·5 per cent. gas was 50 micro-amperes, and this rapidly diminished as the gaseous mixture approached that for theoretical perfect combustion. At 15·8 per cent. the galvanometer reading was approximately one micro-ampere. Above and below this percentage the current increased. Whereas for flame, *ceteris paribus*, the current was 205 micro-amperes for 18·5 per cent. gas; diminishing to 195 micro-amperes for 13 per cent. gas.

The maximum current due to temperature alone both for surface combustion and flame was approximately 3 micro-amperes, obtained by completely sealing similar electrodes in the fire-clay plugs in the same exploring holes. Thus, as might be expected, the conductivity of the fire-clay, at these temperatures, had little influence upon the currents determined. The tubule situated four inches from the inlet to the combustion chamber gave the maximum effects in all cases, the current density falling off on either side of the tubule.

From these results it appears, as might be expected, that the zone of the greatest ionic activity is the tract surrounding the refractory fragments in which the combination of the gases is most active and the temperature of surface combustion highest. Further, the difference between the flame and surface combustion curves may arise from the

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fact that it is extremely difficult to get contact with the surfaces on which surface combustion is being developed. Certainly the gas beyond the surfaces in the space usually occupied by flame, when there is flame combustion, is not so electrically active as when there is surface combustion. This shows that the region of electrical activation of the combining gases is strictly confined to a region of little more than molecular thickness on the porous surfaces of the heated refractory material.

8. The influence of thermionic discharge alone—no inflammable gas present.

As a control experiment the combustion chamber was heated both by surface combustion and by flame up to various temperatures, and when the conditions had become steady, the gas was turned off and air alone was drawn through the apparatus.

In all cases, both the combustion chamber and the tinned-iron box gave evidence of very slight negative electrification. The maximum effect occurred on the tube.

Thus, since the most important effects were of positive electrification on the tube, it is possible to neglect this slight modification due to thermionic discharge. If the effects of thermionic discharge were at all comparable with those due to combustion, the observed loss of charge of the tube, when the gas is cut off and air alone drawn over the heated surface, should be of the same order as that due to combustion. But this is not the case. There is a scarcely perceptible fall of voltage after the gas is cut off. The vessels are so well insulated that the constancy of the charge is a certain indication of the relative importance of direct transfer of negative ions from the heated material to the tube when there is only air present.

Summary of Experimental Results.

1. Sign of electrification of surface combustion alone as distinct from flame.

(a) *Flue Gases.*—Negative for gas percentages less than about 16 per cent., when all trace of electrification disappears. For percentages higher than 16 per cent. the sign is positive. Air is in excess below 16 per cent., gas is in excess above 16 per cent.

(b) *Combustion Chamber.*—The above electrification is reversed. The sign is positive for percentages less than 16 per cent. approximate, owing to the *burning* gases

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carrying a positive charge, as quoted above. The burning gases impinge upon the walls of the chamber, thereby imparting to it their positive charge; while for percentages above approximately 16 per cent. it appears that the *unburnt* gas predominates, imparting a negative charge. When there is perfect combustion there is *no electrification on either*, showing definitely that there is then complete electrical equilibrium between gases and heated surfaces. Thermionic discharge from the combustion tube is negligible.

2. Electrification produced by flame.

(a) *Flue Gases.*—Wholly positive between 2·6 per cent. and 18·5 per cent. gas.

(b) *Combustion Chamber.*—The sign appears to depend on the temperature. Until a certain low temperature is reached (the chamber tube is red hot), the electrification is negative; beyond this it remains positive for the percentages examined.

3. Items 1 and 2, *supra*, stated otherwise:—

The identification of perfect combustion by electrical means is possible.

(a) The *Flue Gases* display increasing electrification from 2·8 per cent. to 9·5 per cent. gas, from which point to 15·8 per cent. the electrification decreases. At 15·8 per cent. gas, the mixture for perfect surface combustion, *no electrification is detectable.* Beyond this value electrification is again apparent. but is of opposite sign.

(b) The *Combustion Chamber* gives evidence of the same series of phenomena, but of opposite sign.

Thus perfect surface combustion may be detected electrically, but the exact conditions are difficult to determine owing to the flatness of the curve connecting rate of charge with percentage. Moreover, elaborate precautions are essential regarding the careful insulation from all metallic contacts and inductive effects of the electrometer used to detect the electrical conditions.

4. If the conductivity of the gases within the combustion chamber during perfect combustion be represented by unity, then the conductivity during flame combustion is found to be approximately 70. This is strong evidence that the added heat of combustion during surface combustion is not due to currents in the metal tube.

5. Thermionic discharge has negligible influence upon the results.

During surface combustion alone the region of most

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intense radiation is appreciably more concentrated towards the combustion chamber inlet than during flame combustion.

The increase of gas from 2·8 per cent. to 16 per cent. produces, in the case of surface combustion, increasing temperature in a small and well-defined region, whereas such an increase in flame combustion results in an appreciably extended region within which combustion is developed.

The author is indebted to Professor Thornton for his active interest in this research.

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XXV. *X-Ray Terms and Intensities.* By H. R. Robinson, *Ph.D., DSc., University of Edinburgh**.

[Plate V.]

I RECENTLY published the results of a series of measurements on the groups of electrons ejected by homogeneous X-rays from a number of elements †. The elements under examination were exposed to an intense beam of copper $K\alpha_1$ X-rays, and the energies of the expelled electrons were deduced from measurements of their trajectories in a uniform magnetic field. Each element gives a characteristic "spectrum" made up of a number

* Communicated by Professor C. G. Barkla, F.R.S.

† Robinson, "The Secondary Corpuscular Rays produced by Homogeneous X Rays," Proc. Roy. Soc. A, civ. p. 455 (1923). For brevity, this paper will be referred to as "R.S. 1."

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of groups of practically homogeneous cathode rays, each group corresponding to one of the "X-ray absorption levels" of the element—*i. e.*, to a term in its X-ray spectrum.

Measurements of these corpuscular spectra provide therefore an independent method of measuring X-ray absorption limits, and I have shown that the method can be successfully applied to regions in which the ordinary methods of X-ray spectrometry break down. Further—which is of greater immediate importance in the theory of atomic structure—the experiments yield fairly precise data as to the relative amounts of absorption of X-rays by the electrons in the different Bohr levels of the atom *.

The experiments to be discussed here are a continuation of those described in R.S. 1, where full experimental details may be found. For a number of reasons the progress of the work has been interrupted, and the results given below refer to experiments which have been carried out at irregular intervals during the past year. The apparatus has been entirely rebuilt, with but slight modification in detail. The Helmholtz-Gaugain double coil has again been used for producing the magnetic field: it has been necessary to use slightly smaller coils—37·5 instead of 39·6 cm. diameter. This change involves a rather greater departure from uniformity of the magnetic field, especially when weaker fields are used to secure greater dispersion. The corrections for inhomogeneity of field and for the stray effect of the compensating coils have, however, been very carefully investigated, and satisfactory consistency has been obtained in the measurements for the same lines in different fields. The mounting of the coils has been improved, and the absolute values of the currents have been measured with greater accuracy. On the whole, therefore, the accuracy of the measurements has been slightly increased, in spite of the use of smaller coils. The construction of new coils has made it possible to re-determine the absolute values of the magnetic fields, and naturally some of the experiments made with the original apparatus have been repeated for comparison. It appears probable that the values of rH given in R.S. 1 were on the average too low by about 1 part in 1000. There were also slight errors in some of the old results for the lines with relatively large rH, in cases where these were not measured in strong fields, on account of insufficient allowance being made for lack of uniformity of field.

* See in this connexion a very interesting paper by E. C. Stoner, Phil. Mag. xlviii. p. 719 (1924).

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The Müller water-cooled X-ray tube * has again been used, with a crude form of mercury vapour pump. The tube has been driven by an induction coil with mercury-gas break and mechanical or point-and-plate rectifier; in a few cases an electrolytic break has been used with good results. It has been found that the ordinary medical type of induction coil is inadequate for the continuous high output required, and the latest experiments have been carried out with a home-made—or rather re-built—induction coil immersed in engine-oil for more efficient cooling.

The following are the additional results obtained with copper $K\alpha_1$ as primary X radiation. The notation is the same as in R.S. 1. r = radius of the path of an electron in a field of H gauss. The kinetic energy of the electron is calculated from the formulæ :—

$$\frac{mv}{e} = rH,$$

where v = velocity and m = mass of electron,
e = charge in E.M.U.

If $\beta = \frac{v}{c}$, where c is the velocity of light,

$$\beta^2 = \frac{(mv/e)^2 \times (e/m_0)^2}{c^2 + (mv/e)^2(e/m_0)^2},$$

where m_0 is the mass of an electron at rest.

Energy of electron $W = m_0c^2\left(\frac{1}{\sqrt{1-\beta^2}} - 1\right)$.

The energies are expressed in terms of the equivalent frequency divided by the Rydberg frequency, *i. e.*

$$\frac{W}{h \times R} = \nu/R,$$

where h = Planck's constant and $R = 109737 \times c$.

The following are the values adopted for the various constants :—

$$e/m_0 = 1{\cdot}7686 \times 10^7 \text{ E.M.U./gramme},$$

$$e = \frac{4{\cdot}774 \times 10^{-10}}{c} \text{ E.M.U.},$$

$$h = 6{\cdot}545 \times 10^{-27} \text{ erg . sec.},$$

$$c = 3 \times 10^{10} \text{ cm./sec.},$$

Copper $K\alpha_1$ $\nu/R = 592{\cdot}8$.

* A. Müller, Phil. Mag. xlii. p. 419 (1921).

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92. Uranium (Oxide).

Remarks.	Intensity.	rH.	ν/R.	592·8 − ν/R.	Origin.	Other values of ν/R.
						Uranium
	3	206·3	276·9	315·9	M_{III}	M_{III} = 317·2
	4	221·4	318·8	274·0	M_{IV}	M_{IV} = 274·0
	5	226·1	332·4	260·4	M_V	M_V = 261·0
	2	273·9	486·8	106·0	N_I	N_I = 106·6
	3	277·7	500·3	92·5	N_{II}	N_{II} = 95·7
	5	282·4	517·3	75·5	N_{III}	N_{III} = 77·1
Double: not quite separated * ...	6	288·7	540·4	52·4	N_{IV}, N_V	N_{IV} = 56·3 N_V = 53·6
	2–3	292·8	555·8	37·0	Oxygen K?	Oxygen K = 36·8 †
Head of a narrow band	3	295·7	566·8	26·0	N_{VI}, N_{VII}, O_I	N_{VI} = 28·4 N_{VII} = 27·6 O_I = 26·2
	2	298·4	577·1	15·7	O_{II}, O_{III}	O_{III} = 12·4
Head of a narrow band	2–3	301·7	589·9	2·9	O_{IV}, O_V, P	P = 2·1

* When two lines are too close to be separated, only the one with larger rH can be measured—*i. e.*, the one corresponding to the smaller term in the X-ray spectrum.

† Mean of values: Kurth, Mohler and Foote.

90. Thorium (Nitrate).

Remarks.	Intensity.	rH.	ν/R.	592·8 − ν/R.	Origin.	Other values of ν/R.
						Thorium
	1	181·0	213·3	379·5	M_I	M_I = 381·6
	1	191·1	237·7	355·1	M_{II}	M_{II} = 354·4
	3	213·2	295·8	297·0	M_{III}	M_{III} = 298·0
	4–5	226·8	334·5	258·3	M_{IV}	M_{IV} = 256·6
	5–6	231·5	348·3	244·5	M_V	M_V = 244·9
	2	276·1	494·6	98·2	N_I	N_I = 97·8
	2–3	279·5	506·8	86·0	N_{II}	N_{II} = 90·2
	3–4	284·2	523·8	69·0	N_{III}	N_{III} = 71·2
Double: not quite separated	5	289·8	544·4	48·4	N_{IV}, N_V	N_{IV} = 51·2 N_V = 48·7
	3	293·0	556·4	36·4	Oxygen K	Oxygen K = 36·8
Narrow band.....	2–3	296·1	568·4	24·4	N_{VI}, N_{VII}, Nitrogen K	N_{VI} = 24·8 N_{VII} = 24·0
	2	298·2	576·5	16·3	O_I?	——
	3	301·7	590·1	2·7	P	P_I = 2·1

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79. Gold (Leaf).

Remarks.	Intensity.	rH.	ν/R.	592·8 − ν/R.	Origin.	Other values of ν/R.
						Gold
	2	228·6	339·8	253·0	M_I	M_I = 252·9
	3	235·8	361·4	231·4	M_{II}	M_{II} = 235·1
	6	245·6	391·9	200·9	M_{III}	M_{III} = 202·8
	6	255·8	425·1	167·7	M_{IV}	M_{IV} = 169·3
	6	257·8	431·6	161·2	M_V	M_V = 163·0
	3	287·7	536·7	56·1	N_I	N_I = 58·0
	4	290·1	545·7	47·1	N_{II}	N_{II} = 49·1
	4	292·3	553·9	38·9	N_{III}	N_{III} = 42·8
Narrow band (double).	5	296·2	568·6	24·2	N_{IV}, N_V	N_V = 25·0
Narrow band.....	3	301·6	589·5	3·3	N_{VI}, N_{VII}, O	O_V = 0·8

33. Arsenic (Oxide).

Remarks.	Intensity.	rH.	ν/R.	592·8 − ν/R.	Origin.	Other values of ν/R.
						Arsenic
	6	272·2	480·8	112·0	L_I	——
Inaccurate: not quite resolved.	6?	275·2	491·4	101·4	L_{II}	L_{II} = 100·7 *
	6	276·5	496·0	96·8	L_{III}	L_{III} = 98·4 *
Inaccurate: edge diffuse.....	2	292·8	555·8	37·0	Oxygen K	Oxygen K = 36·8
Narrow band: diffuse edge ...	3–4	299·8	582·5	10·3	M	M_{III} = 11·2 *

* Interpolated from Walter, *loc. cit.*

25. Manganese (Oxide).

Remarks.	Intensity.	rH.	ν/R.	592·8 − ν/R.	Origin.	Other values of ν/R.
						Manganese
Inaccurate: on two plates only. Doubtful line.	1	131·4	112·7	480·1	K	K = 482·4
Head of a broad band	6	243·2	384·3	—	Fluorescent K-L etc.	384·3 = MnKα_1* − 51·1
Head of a band: diffuse	3	258·4	433·6	—	Fluorescent K-L etc.	433·6 = MnKβ_1* − 45·5
Inaccurate: barely resolved	4	287·9	537·5	55·3	L_I	——
	2	289·9	544·9	47·9	L_{II} / L_{III}	L_{II} = 48·7 / L_{III} = 47·9
	2	292·9	556·1	36·7	Oxygen K	Oxygen K = 36·8
Narrow band: diffuse.....	2	301·6	589·5	3·3	M	——

* Manganese Kα_1, ν/R = 435·4: Kβ_1, ν/R = 479·1.

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22. TITANIUM (Oxide).

Remarks.	Intensity.	rH.	ν/R.	592·8 − ν/R.	Origin.	Other values of ν/R. Titanium
	3	187·2	228·3	364·5	K	K=365·4
Head of a band.....	4–5	213·9	297·5	—	Fluorescent K-L etc.	297·5=TiKα_1 * −34·8
Band	2	226·3	333·0	—	Fluorescent K-L etc.	333·0=TiKβ_1 * =30·2
Band	3	251·8	411·8	—		
Band	2–3	266·4	460·6	—		
Band	4	292·8	555·8	37·0	TiL Oxygen K	L_{III}=32·2

* Titanium Kα_1, ν/R=332·3: Kβ_1, ν/R=363·2.

The values of ν/R given for comparison have generally been taken from the tables of Bohr and Coster †. Other tables of X-ray terms have appeared more recently—*e. g.* those given by Hjalmar ‡, Walter §, and Nishina ‖ ; these do not, however, differ very greatly from the tables of Bohr and Coster, even for terms which in the earlier tables had to be obtained by interpolation. In any case the Bohr and Coster values are sufficiently accurate for the present purpose.

The "intensities" are again estimated on a 1–6 scale, 6 being the strongest.

It will be seen that the general nature of the distribution of intensity among the sub-groups follows closely the lines indicated in R.S. 1 ; taken in conjunction with the older experiments, the present set show quite clearly that so long as the critical absorption frequency of a group is not too far removed from the frequency of the incident radiation, most of the secondary electrons emitted come from the "softer" sub-groups (*i. e.* those with higher suffixes in Bohr's notation). Taking, however, groups with smaller and smaller critical absorption frequencies, a progressive change is observed in the distribution among the sub-groups; this consists in a gradual transference of the maximum intensity from the "softer" to the "harder" members of the group. There is now no doubt that this holds generally in the M and N as well as in the L sub-groups. Similar effects are cited

† Bohr & Coster, *Zeitsch. f. Physik*, xii. p. 342 (1923).
‡ E. Hjalmar, *ibid.* xv. p. 65 (1923).
§ B. Walter, *ibid.* xxx. p. 357 (1924).
‖ Y. Nishina, Phil. Mag. xlix. p. 521 (1925).

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by Ellis and Skinner * in the case of the β rays excited by γ rays. The same effect is also shown in a rather different way in some other experiments by Skinner †. In these experiments Skinner photographed the fluorescent L-spectrum of cerium when excited by primary X-rays varying in wave-length from approximately 0·6–1·5 Å.U. He found that as the wave-length of the exciting radiation was diminished, the cerium emission lines belonging to the L_I sub-group gradually increased in intensity relatively to those of the L_{II} and L_{III} sub-groups. These results completely confirm the view expressed in R.S. 1, p. 475, that the probability of the ejection of an electron from a given sub-group is governed by other factors than the simple number of electrons in that subgroup. This is clearly a point of great intrinsic interest: it seriously complicates, however, the problem of obtaining evidence from the corpuscular spectra about the distribution of electrons among the subgroups (*cf.* Stoner, *loc. cit.* p. 732). The experiments in which only copper K rays are used are necessarily restricted in range, and in order to extend this range experiments have been begun with molybdenum K rays; it is hoped that the results of these will soon be available for publication. Another experimental disadvantage which accompanies the use of a soft primary radiation like copper K has been brought out clearly in the present experiments. The photographic plates employed show a marked diminution in sensitivity for electrons with energies corresponding to ν/R less than about 200. Thus the calcium and sulphur K levels appear very readily on the plates, about equal in intensity (using a $CaSO_4$ target). Titanium K is appreciably less intense, and vanadium K very faint. Manganese K has been identified on two plates only, and that with no great certainty, in spite of some very prolonged exposures. The manganese K level would be expected to be a very efficient absorber of copper K radiation, and there is in fact ample evidence of this on the plates; by far the strongest line observed here is a "fluorescent" line due to the fluorescent K rays excited in the target itself (see table of results). Of course slow electrons are in any case at a disadvantage as compared with faster ones, as they can only escape from very small depths in the target, but the photographic plate is also responsible for the feebleness of these lines. The effect cannot be due to scattering by residual gas in the

* C. D. Ellis and H. W. B. Skinner, Proc. Roy. Soc. A, cv. p. 186 (1924).

† H. W. B. Skinner, Proc. Camb. Phil. Soc. xxii. p. 379 (1924).

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camera, as such low-velocity lines as have been obtained are equally sharp whether recorded in strong or in weak magnetic fields: *i. e.* the sharpness of the lines is independent of the length of the path travelled in the camera.

The same reason probably accounts for the complete failure to observe the M_I and M_{II} lines of uranium. In any case these lines would be expected to be very faint, but they should be detectable. I have searched for these on a large number of plates, without getting sufficiently definite evidence. There are always a number of slight gradations of intensity in the plates, which might possibly be interpreted as spectral lines,—and some of them undoubtedly correspond to faint lines in the fluorescent corpuscular spectra, or possibly to electrons extracted from multiply-ionized atoms, as suggested by Wentzel *. I have felt it safer to ignore "lines" of this type. With thorium, I have fortunately two plates in which M_I and M_{II} stand out fairly clearly, so have been able to include these lines, though without much confidence as to their accuracy. It seems likely that better results would be obtained with Schumann plates in the region of low-velocity electrons †.

There are a few points to be mentioned in connexion with the estimates of intensity, though a detailed discussion is best postponed until the completion of the work with molybdenum rays, in which the complication of variation in photographic sensitivity should be less troublesome. In the present work, the visual estimates of intensity have been supplemented by photometric records. These records were taken with the photoelectric cell photometer used by Professor R. A. Sampson in his work on stellar spectra ‡, and I am deeply indebted to Professor Sampson for permission to use the instrument, and to Mr. E. A. Baker for making the records. The comparison of the visual estimate with the photometer records has been most interesting. The most obvious difference is that the eye seems rather more impressed than the photometer by differences in intensity. Thus, compared with the photometer, the visual estimates somewhat exaggerate the differences in intensity. It must of course be remembered that the photometer is just as arbitrary in its judgments as the human eye, though it may be more consistent.

Records of two plates taken under identical conditions with a gold target are reproduced in Plate V. fig. 1, the

* G. Wentzel, *Ann. d. Phys.* lxvi. p. 437 (1921).

† *Cf.* J. A. Becker, Phys. Rev, xxiv. p. 478 (1924).

‡ R. A. Sampson, Monthly Notices R. A. S. lxxxiii. p. 174 (1923).

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two records being placed together for comparison. The high-velocity end of the spectrum is on the left, and the extreme sharpness of the high-velocity edges of the lines is well brought out in the records. (The slight deviation of the trace from the vertical is partially attributable to the finite width of the photometer slit.) The small serrations in the trace are due to the granulations in the photographic emulsion (both plates were over-developed almost to the commencement of chemical fog). Considering the lower record, which is the clearer of the two, reading from right to left, we have M_I and M_{II} appearing as two small humps, then M_{III} as a very well-marked hump. M_{IV} and M_V are clearly separated, though not very far apart: the distance between the two high-velocity edges in the original negative is 0·85 mm. Following M , after a space N_I, N_{II}, N_{III} appear together in a broad hump (one of the four "notches" shown in the group is accidental, and does not appear on other records), N_{IV} and N_V incompletely separated in a narrower hump, and finally the N_{VI}, N_{VII}, and O lines all together. The same lines can be seen less clearly in the upper record.

A comparison of the two records shows the different characteristics of the two kinds of plate used. The lower one is from an Ilford Process Plate, the upper an Ilford X-ray Plate—the latter possibly over-exposed. Although the lower plate gives a much clearer record, there is very little to choose between them for measurements under the micrometer.

The photometer curves bring out very clearly the diffuse nature of the low-velocity sides of the lines—partly due to the geometry of the apparatus, but mainly to the "straggling" of the electrons from the deeper layers of the target. Visually, the lines of the corpuscular spectrum appear well under 1 mm. in width, except in the case of very strong lines; the diffuseness of the low-velocity edges is obvious, but not very obvious to casual inspection. The photometer shows the effect stretching for several centimetres along the plate (this is more clearly shown in other records, where the lines are fewer and more widely spaced, as in the case of a calcium-sulphate target). The low-velocity end of the plates is thus always more or less fogged by straggled electrons belonging to the groups at the high-velocity end. This feature of the photographs was recognized from the first *, but, as Stoner points out (*loc. cit.* p. 733), it may not have been sufficiently emphasized.

* Robinson and Rawlinson, Phil. Mag. xxviii. p. 280 (1914).

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The actual photographs, though very clear, are not in general suitable for reproduction. The lower plate of fig. 1 has, however, been reproduced in fig. 2. My friend Mr. Drummond Young very kindly placed his considerable skill in photographic work at my disposal, and obtained this print after intensifying the original plate with mercuric chloride *. The prints in my possession are extremely beautiful, and show all the detail given in the table of results, including the separation of N_I, N_{II}, and N_{III}: they may, in the nature of things, lose some detail in a further reproduction. As in the case of the photometer curves, the high-velocity edge is to the left. This reproduction is from an original negative on a "Process" plate. It is worthy of note that a reproduction from a similar photograph on an X-ray plate (corresponding to the upper photometer curve) shows the strong lines of the N group about equally intense with M_{IV} and M_V (*cf.* R.S. 1, p. 474).

I wish to express my thanks to Professor Barkla for providing facilities for this work and for his interest in its progress; also to the Committee of the Moray Research Fund for a grant towards the purchase of apparatus and materials.

University of Edinburgh,
March 31, 1925.

XXVI. *On the Statistical Theory of Emission of Electrons from Hot Bodies.* By S. C. Roy, *M.Sc., Ghose Research Scholar in Physics, University College of Science, Calcutta* †.

§ 1. *Introduction.*

It is well known that the classical electron theory of metallic conduction, as developed by Drude, Lorentz, Thomson, and others, is inadequate to give a satisfactory and consistent account of the various outstanding physical properties of metals such as their specific heats, their optical properties, and supraconductivity. In fact, the difficulty of working out a correct law of radiation on the basis of the law of equipartition for the motion of the metallic electrons compels us to abandon the classical theory.

On the other hand, there is an impression that the facts of the thermionic emission of electrons from hot bodies favour

* The photometer record was made before the intensification.

† Communicated by Mr. R. H. Fowler, M.A.

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the kinetic electron theory. This impression is probably due to the fact that a fairly satisfactory representation of the phenomenon is given by the law of emission,

$$I = A \cdot T^{1/2} \cdot \epsilon^{-b/T},$$

as originally deduced by Richardson * on the supposition that the electrons both inside and outside a hot body are governed by the same laws of classical dynamics. This fact, however, cannot be accepted as proving the validity of the classical electron theory of metals. As a matter of fact, the experimental results of Davisson † and Germer on the latent heat of electron emission, as measured by the cooling effect, are definitely against the classical theory of metallic conduction. Their measurements lead to the conclusion that electrons inside the metals possess zero or negligible kinetic energy. We are thus forced to abandon the law of equipartition for the motions of the metallic electrons and to adopt Planck's law of quanta as governing their energy-content. We therefore suppose that the metallic electrons, instead of forming an ideal gas, constitute a condensed solid and are distributed in space-lattices like the atoms in a crystal. In a previous paper ‡ I pointed out that one can use these ideas in deriving a law of emission of the form

$$I = AT^2\epsilon^{-b/T},$$

where A is a universal constant equal to $2\pi mek^2/h^3$, provided the electron frequencies be so large as to make $h\nu$ large compared to kT.

In the course of this paper, I propose to present this law as a theorem in statistical mechanics modified to include the modern quantum theory and to show that the law takes the same form if the mechanism of emission be supposed to be radiative. The machinery required for the statistical calculations has been completely set up by Darwin and Fowler in a series of papers §. One has simply to transcribe their results in terms of electrons to obtain the thermionic law of emission. The application of this new method of statistical mechanics to the present problem brings out into clearer view all the assumptions involved.

* Camb. Phil. Proc. ii. p. 286 (1901).

† Phys. Rev. xx. (1922).

‡ Phil. Mag. xlvii. p. 261 (March 1924).

§ Darwin & Fowler, Phil. Mag. xliv. pp. 450, 823 (1922), papers 1 and 2; Proc. Camb. Phil. Soc. xxi. p. 262 (1922), paper 3; p. 392 (1923), paper 6; Fowler, Phil. Mag. xlv. pp. 1, 497 (1923).

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In the next paragraph, therefore, I shall give an account of the new method and the principal results in as much detail as is necessary to understand their salient features, and then adopting some of the results proceed directly to the deductions of the law of emission.

§ 2. *Summary of the New Method of Statistical Mechanics and its Principal Results.*

In a series of papers * Fowler and Darwin have discussed at length the general distribution laws of an assembly of various systems by a special method. The essential feature of the new method is the calculation of Averages by means of Integrals whose Integrands are simply expressed in terms of certain functions which they call partition-functions, equivalent to the "Zustand-Summe" of Planck.

For every type of systems in an assembly, quantized or classical, there exists a partition function which depends on the motion of that system alone so long as it is not too frequently interfered with. Such an assumption of limited interference is fundamental in all statistical calculations. This function is originally defined for quantized systems, and is then extended by a limiting process to systems obeying classical laws. All the physically possible states of the system are enumerated. These form a series of discrete states for a quantized system with energies $\epsilon_0, \epsilon_1, \epsilon_2 \ldots$ etc., having weights (*à priori* possibilities) $p_0, p_1, p_2 \ldots$ etc., and the partition-function is defined as a function of a complex variable Z by the equation

$$f(Z) = \Sigma_r p_r Z^{\epsilon_r}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

summed over all permissible states.

The partition-function for a group of N such systems is $[f(Z)]^N$. For the classical systems obeying Hamiltonian equations, the available phase-space is divided into cells whose dimensions are ultimately made to tend to zero, the weight attached to any cell being proportional to its extension. The summation (1) is replaced by an integral, and it is shown that this limit can be used in all formulæ without any restriction.

It is next shown that, for every group of systems in an assembly in statistical equilibrium, the parameter Z must have a unique real value ϑ, which is the temperature of the assembly measured on a special scale, and is related to

* *Loc. cit.*

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the absolute temperature of the second law of thermodynamics as follows:

$$\vartheta = \epsilon^{-1/kT}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The mathematical principles employed for obtaining adequate approximations are the Multinomial theorem, and the method of Asymptotic expansion by steepest descents. The conditions and the range of applicability of these theorems to statistical calculations have been fully discussed by the two authors.

I will relate here some of the typical results which apply directly to the deduction of the thermionic law of emission. The partition function for a Planck's line vibrator, which takes energy in multiples of quanta $\epsilon = h\nu$, is

$$f(\vartheta) = \frac{1}{1-\vartheta^{\epsilon}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The partition-function for a free monatomic molecule of mass m confined in a volume V is,

$$\mathrm{H}(\vartheta) = \frac{(2\pi m)^{3/2} . \mathrm{V}}{h^3 [\log 1/\vartheta]^{3/2}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The partition-function for temperature radiation has also been constructed. The radiant energy is regarded as the energy of a single system, æther, which is in general heavily degenerate; but for purposes of statistical calculations all questions of degeneracy are ignored on reasonable grounds, and the partition-function for the radiant energy contained in a volume V takes the form

$$\mathrm{R}(\vartheta) = \exp. \frac{8\pi^5 . \mathrm{V}}{45 c^3 h^3 (\log 1/\vartheta)^3}. \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The same method has enabled the authors to translate Born's results on the mean energy of a crystal into results of partition-functions $\mathrm{K}_1(\vartheta)$. Setting aside the higher frequencies due to the motions of the electrons as distinct from the complete atoms,

$$\log \mathrm{K}_1(\vartheta) = -\frac{3}{\log (1/\vartheta)^3} \cdot \sum_{j=1}^{3} \frac{1}{k^3 \Theta_j^3} \int_0^{k\Theta_j \log 1/\vartheta} x^2 \log (1-\epsilon^{-x})\, dx$$
$$- \sum_{j=4}^{3(S-1)} \log (1-\vartheta^{h\nu_j}), \quad (6)$$

where S is the number of atoms in the elementary cell of the atomic space-lattices of the crystal, and Θ_j and ν_j are constants characteristic of the crystal.

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In any discussion in which the atoms are considered to be the only structural units, one can legitimately ignore the electrons, but if one imagines the solid to be constituted of independent atomic and electronic space-lattices, one cannot afford to leave the electron frequencies out of consideration. The partition-function of the electronic lattices, however, is easily constructed in the form

$$\log K_2(\vartheta) = -\sum_{j=1}^{3n} \log (1-\vartheta^{h\nu_j}), \quad . \quad . \quad . \quad (7)$$

where n is the number of electrons contained in each lattice.

§ 3. *Application of this Method to the Phenomenon of Electron Emission from Hot Bodies.*

In the present problem, we have to consider the temperature equilibrium of a hot metal crystal with the radiant energy of the æther and with an atmosphere of gaseous free electrons confined in an enclosure of volume V. The metal crystal is itself constituted of two different systems—atomic (ionic) lattices and electronic lattices; so that the assembly for our statistical calculations embraces four different types of systems—æther, free electrons, electronic lattices, and atomic space-lattices. To ensure no loss of generality we should formally include all the four systems in our statistical considerations. It is, however, implied that in the specified assembly the atomic lattices preserve their individualities.

Let us suppose that in any example of the assembly we have N free gaseous electrons, genuinely mon-atomic, and M electronic lattices each containing n electrons and a number S of the atomic lattices which remains constant in all such examples. We have first to determine the total number of essentially different ways in which such examples of the assembly may be built up out of a total of X equal to $(N+M\,.\,n)$ electrons, the other systems—atomic lattices and æther—remaining undisturbed. Each time we choose a group of N electrons out of the total number X for the vapour-phase, we are left with $M\,.\,n=(X-N)$ electrons to be arranged in lattices inside the metal crystal. The total number of different ways in which the X electrons can be divided into two groups of N and $(X-N)$ is equal to

$$\overset{X}{C}_N = \frac{X!}{N!(X-N)!} \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

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Now, since the present method * of calculation of the partition-function for the translational motion of the gaseous electrons allows for all possible interchange of positions amongst them, any one group of N electrons in the vapour phase cannot be permuted over again to yield more than one distinct mode of forming the assembly. But any group of $(X-N)$ electrons in the condensed phase can be arranged in lattices in $(X-N)!$ ways, and each of these arrangements corresponds to an essentially different mode of building the metal crystal. Hence the total number of essentially different ways of forming the specified assembly is proportional to

$$C_N^X \cdot P_{(X-N)}^{(X-N)} = \frac{X!}{N!}, \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where $X = N + M \cdot n$ = constant.

Next, let us define the state of zero energy of the assembly to be that in which all the free electrons have zero kinetic energy and all other systems of the assembly are in their lowest quantum state. Let χ be the work necessary to remove one electron out of the crystal to the free state with zero kinetic energy, the assembly being in zero state of energy as defined above. χ in fact corresponds to what may be called the latent heat of evaporation of an electron at the absolute zero of temperature. If E be the total energy for any example of the assembly relative to the conventional zero, then the energy available for distribution among the partition-functions with N free gaseous electrons is given by

$$F = E - N\chi. \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

But the number of weighted complexions c for any example of the assembly of S atomic lattices, M electronic lattices, N free electrons, and æther in a volume V with energy F available for distribution is given by

$$c = \frac{1}{2\pi i}\int_\gamma \frac{dZ}{Z^{F+1}} \cdot R(Z) \cdot [K_1(Z)]^S \cdot [K_2(Z)]^M \cdot [H(Z)]^N$$

$$= \frac{1}{2\pi i}\int_\gamma \frac{dZ}{Z^{E+1}} \cdot R(Z) \cdot [K_1(Z)]^S \cdot [K_2(Z)]^M \cdot [H(Z) \cdot Z^\chi]^N; \quad . \quad . \quad . \quad (11)$$

the contour γ is any circle round the origin of radius less than unity. The number of such examples of the assembly

* *Cf.* footnote, p. 743, of Darwin and Fowler's paper on "Some Refinements of the Theory of Dissociation Equilbria," Proc. Camb. Phil. Soc. xxi. part 6 (1923).

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being proportional to $1/N!$, the total number of weighted complexions is proportional to C, where

$$C = \frac{c}{N!} = \frac{1}{2\pi i}\int_\gamma \frac{dZ}{Z^{E+1}} \cdot R(Z) \cdot [K_1(Z)]^S \cdot [K_2(Z)]^{X/n} \sum_{N=0}^{N=X} \frac{\beta^N}{N!}, \quad . \quad . \quad . \quad (12)$$

$$\beta = \frac{H(Z) \cdot Z^X}{[K_1(Z)]^{1/n}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

If X and E be taken sufficiently large and n a small integer, all the conditions laid down by Fowler and Darwin for the evaluation of such integrals are satisfied. The asymptotic expansion of $\sum_{N=0}^{N=X} \frac{\beta^N}{N!}$ is exp. β.

Also we have

$$CN = \frac{1}{2\pi i}\int_\gamma \frac{dZ}{Z^{E+1}} \cdot R(Z) \cdot [K_1(Z)]^S \cdot [K_2(Z)]^{X/n} \cdot \sum_{N=0}^{N=X} \frac{N\beta^N}{N!}$$

$$= \frac{1}{2\pi i}\int_\gamma \frac{dZ}{Z^{E+1}} \cdot R(Z) \cdot [K_1(Z)]^S \cdot [K_2(Z)]^{X/n} \cdot \beta \cdot \exp. \beta. \quad . \quad . \quad . \quad (14)$$

It now easily follows that

$$\bar{N} = \beta(\vartheta) = \frac{H(\vartheta) \cdot \vartheta^X}{[K_1(\vartheta)]^{1/n}}, \quad . \quad . \quad . \quad . \quad (15)$$

wherein ϑ and E are related by the equation

$$E = \vartheta \frac{\partial}{\partial \vartheta} \log R(\vartheta) + S\vartheta \frac{\partial}{\partial \vartheta} \log K_1(\vartheta) + M\vartheta \frac{\partial}{\partial \vartheta} \log K_2(\vartheta)$$
$$+ \bar{N}\vartheta \frac{\partial}{\partial \vartheta} \log H(\vartheta) + \bar{N}\chi. \quad (16)$$

The relation (15) on substitution gives

$$\bar{n} = \frac{\bar{N}}{V} = \frac{(2\pi mkT)^{3/2}}{h^3 K_2(T)} \cdot \epsilon^{-\chi/kT}, \quad . \quad . \quad . \quad (17)$$

where $\bar{n}$ is the average number of free electrons per unit volume in the temperature equilibrium with the hot metal. The thermionic current* per second per unit area is therefore

* If allowance is to be made for the reflexion of electrons from metals, the expression for I has to be multiplied by $(1-r)$, where r is the fraction of the incident electrons sent back by reflexion. For most metals r has the value near ·5 (Gehrts, *Ann. der Phys.* xxxvi. p. 995, 1911). This fact, if taken into account, would reduce the universal constant to half its value.

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equal to

$$I = \bar{n} \cdot e\left(\frac{kT}{2\pi m}\right)^{1/2} = \frac{2\pi mek^2}{h^3 K_2(T)} \cdot T^2 \cdot \epsilon^{-\chi/kT}. \quad . \quad (18)$$

On *à priori* ground, we cannot, probably, neglect the energy-content of the electron-lattices at all temperatures and put function $K_2(T)=1$. According to Haber's law, electronic and atomic frequencies are related to one another by the equation

$$\frac{\nu_e}{\nu_a} = \left(\frac{m_a}{m_e}\right)^{1/2}.$$

The general space-lattice theory of Born also confirms this law. One cannot, however, deny the approximate nature of this law. But in any case this relation points out that the electronic frequencies are much higher than the atomic frequencies. One can also gather some idea of the electronic frequencies from another consideration. It is well known that the specific heats of metals exceed the Dulong-Petit's limit 3R at high temperatures. For example, the specific heat * at constant volume for potassium at 300° A. is about 0·56 calorie above Dulong-Petit's value 3R. This excess must, then, represent the thermal energy of the electrons. One can therefore roughly estimate the order of the electronic frequencies on the supposition that the excess of specific heats of metals at high temperatures over Dulong-Petit's value is contributed by the vibrating electrons according to Planck's quantum law, and can use as a first approximation Einstein's simple expression

$$C_{v\,\text{elec.}} = 3R \cdot \frac{x \cdot \epsilon^x}{(\epsilon^x - 1)^2},$$

where

$$x = \frac{h\nu}{kT}.$$

Below are given the values of electronic frequencies of some metals roughly estimated from specific heat data † :—

Metals.	Electronic Frequency.
K	$2 \cdot 10^{13}$
Na	$3 \cdot 10^{13}$
Al	$1{\cdot}5 \cdot 10^{14}$
Ni	$1{\cdot}7 \cdot 10^{14}$
Cu	$2{\cdot}0 \cdot 10^{14}$
Ag	$2{\cdot}2 \cdot 10^{14}$

* Lewis & Adams, Phys. Rev. iv. p. 331 (1914). Latimer, Phys. Rev. xliii. p. 818 (1921).

† Koenigsberger, *Zeitsch. Electrochem.* xvii. p. 289 (1911). Lewis, Adams, & Latimer, *loc. cit.*

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No reliance can, probably, be laid upon the actual numerical figures quoted above. But they show that the function $K_2(T)$ cannot differ much from unity even up to the melting-point of these metals. So that for all practical purposes we can regard $K_2(T)$ as equal to unity in the equation (18).

§ 4. *Photo-electric Theory of Emission.*

It is of considerable interest to look at the problem from another point of view. For a statistical theory of emission it is immaterial whether the mechanism of emission be radiative or a collision one. It is, however, very probable, as Wilson * pointed out, that the thermionic emission of electrons is really due to the radiation of the hot body itself. The argument against this view is that the magnitude of the auto-photo-electric currents determined experimentally is much lower than the thermionic currents. This is to be expected, for by impinging radiation from outside on metals we do not really attain to the condition of radiation due to the hot body itself.

If the emission of the electrons be supposed to be due to radiation in equilibrium with the hot body, then one † can show, on the basis of the theory of unit mechanism, $\frac{1}{2}mv^2+\chi=h\nu$, as developed by Kramers ‡ and Milne § that the law of thermionic emission is the same as given by the equation (18).

To adapt Kramer's reasoning to the present problem, it is necessary to modify our idea of the metallic electrons. We have to suppose that they exist in some modified quantized orbits, and constitute Bohr vibrators instead of Planck's line-vibrators.

We start by supposing that the hot body is in a field of "black radiation" at temperatures T° A., and that there exists inside the hot body a state of dynamical equilibrium of radiation such that the amount of energy gained at any

* *Ann. der Phys.* xlii. p. 1154 (1913); Roy. Soc. Proc. A, xciii. p. 359 (1917).

† Since this paper was written, Prof. O. W. Richardson has given a very interesting and illuminating discussion on the Photo-electric Theory of Emission, essentially on the same line (Proc. Phys. Soc. Lond. xxxvi. August 1924), and has considered emission from systems with multiple thresholds. His assumptions regarding the chance of capture of an electron by the atom are, however, different from the simple one adopted here. So he obtains an expression for emission of electrons slightly different from the one considered here [equation (47), p. 394]. His expression, however, agrees in form with the one deduced here.

‡ Phil. Mag. xlvi. p. 840 (1923).

§ Phil. Mag. xlvii. p. 209 (1924).

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instant by any portion of the hot body by absorption of radiation is exactly balanced by the amount lost by it by emission of radiation. We next adopt the supposition that the absorption or emission of radiation by matter takes place in quanta, and is an additive effect of the actions of individual atoms. The absorption by an atom of a radiation quantum (if large enough to provide for energy necessary to release an electron from the restraining forces) results in the expulsion of an electron from the atom, while the emission of the radiation-quantum is attended by the binding of an electron to the atom. If these two processes of energy-exchange be completely reversible, then, in the steady state of radiation, the rate of photo-electric captures of electrons in any volume V inside the hot body must be exactly equal to the rate of photo-electric ejections of electrons.

The unpolarized radiation between the stretch of frequencies ν and $\nu+d\nu$ emitted through a surface element $d\sigma$ of the hot body in time dt in the cone of solid angle $d\omega$ is equal to

$$2 \,.\, dt \,.\, d\sigma \,.\, \cos\theta \,.\, d\omega \,.\, K_\nu \,.\, d\nu, \quad . \quad . \quad . \quad (1')$$

where θ is the angle between the normal to $d\sigma$ and the axis of the cone, and K_ν is defined by Planck * as the specific intensity of radiation of frequency ν.

In the same way we can write for the number of electrons emitted in time dt through $d\sigma$ in the cone $d\omega$ in the direction θ by the stretch of radiation between ν and $\nu+d\nu$ the expression

$$dt \,.\, d\sigma \,.\, \cos\theta \,.\, d\omega \,.\, F_\nu \,.\, d\nu, \quad . \quad . \quad . \quad . \quad (2')$$

where F_ν may be defined as the specific intensity of photo-electric ejection of electrons.

In the steady state the radiant energy emitted or absorbed in volume V of the hot body in time dt between the frequency range ν and $\nu+d\nu$ is

$$dt \,.\, V \,.\, N\alpha_\nu \,.\, 8\pi \,.\, K_\nu \,.\, d\nu, \quad . \quad . \quad . \quad . \quad (3')$$

where N is the number of atoms per unit volume and α_ν is the atomic aborption-coefficient of radiation. The coefficient α_ν needs a word of explanation. It has the dimensions of an area, and may be interpreted as the "effective cross-section" of the atom which absorbs all the radiation of frequency ν impinging on its surface, so that $V \,.\, N \,.\, \alpha_\nu$ represents the total effective area presented by all the atoms in volume V to the absorption of radiation of the same frequency.

* Planck, 'Warme Strahlung.'

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The total number of quanta absorbed in the specified volume in time dt is equal to

$$\frac{dt \,.\, \mathrm{V} \,.\, \alpha_\nu \,.\, 8\pi \,.\, \mathrm{K}_\nu \,.\, d\nu}{h\nu}. \quad . \quad . \quad . \quad . \quad (4')$$

The expression (4′) represents the number of photo-electric ejections of electrons in volume V in time dt by the absorption of radiation between the frequency range ν and $\nu + d\nu$. This number is also given by the expression,

$$dt \,.\, \mathrm{V} \,.\, \mathrm{N} \,.\, \beta_\nu \,.\, 4\pi \,.\, \mathrm{F}_\nu \, d\nu, \quad . \quad . \quad . \quad . \quad (5')$$

where β_ν is the atomic absorption-coefficient of electrons. This coefficient β_ν may be interpreted as follows:—Each atom acts as a sphere of cross-section β_ν such that a free electron is bound to the atom with the emission of radiation only if it strikes this area.

Equating (4′) and (5′) we get a relation between K_ν and F_ν as follows:

$$\mathrm{F}_\nu = 2 \,.\, \frac{\alpha_\nu}{\beta_\nu} \,.\, \frac{\mathrm{K}_\nu}{h\nu}. \quad . \quad . \quad . \quad . \quad . \quad (6')$$

The physical meaning of relation (6′) is that the number of electrons emitted by radiation ν is directly proportional to the intensity of radiation K_ν and inversely proportional to the size of the quantum if α_ν/β_ν were constant.

The quantum theory tells us nothing about the mechanism of absorption or emission of radiation, so that we cannot calculate the coefficients α_ν and β_ν directly. But the process of absorption of radiation by the atoms with the consequent ejection of electrons, and the reverse process of binding of electrons in an atom with the simultaneous emission of radiation, must be governed by the laws of probability in the same manner as absorption and emission of radiation are treated in Einstein's theory of temperature-radiation. On the basis of such probability considerations Kramers has, in developing a theory of absorption of X-rays, obtained a relation between α_ν and β_ν in the form *

$$\frac{\alpha_\nu}{\beta_\nu} = \frac{mc^2}{ah^2\nu^2} \cdot \tfrac{1}{2} m v^2 = \frac{mc^2}{ah^2\nu^2} \cdot (h\nu - \chi), \quad . \quad . \quad (7')$$

where a is a numerical constant†. Using the above expression

* Kramers, *loc. cit.* equation (17), p. 843.

† The numerical factor a is determined by the "*à priori* probability" of an electron remaining bound to the atom.

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for α_ν/β_ν in relation (6′),

$$F_\nu = \frac{2mc^2}{ah^3\nu^3} \cdot K_\nu \cdot (h\nu - \chi). \quad . \quad . \quad . \quad . \quad (8')$$

Now, in the high-frequency region

$$K_\nu = \frac{h\nu^3}{c^2} \cdot \epsilon^{-h\nu/kT}. \quad . \quad . \quad . \quad . \quad . \quad (9')$$

Hence we have

$$F_\nu = \frac{2m}{ah^2} \cdot (h\nu - \chi) \cdot \epsilon^{-h\nu/kT}. \quad . \quad . \quad . \quad (10')$$

Substituting this expression for F_ν in (2′) and integrating, we obtain for the number of electrons emitted from unit area in unit time by radiation of frequency range ν and $\nu + d\nu$,

$$dn = \frac{2m}{ah^2}(h\nu - \chi) \cdot \epsilon^{-h\nu/kT} d\nu \cdot \int_0^1 dt \int_0^1 d\sigma \int_0^{2\pi} d\phi \int_0^{\pi/2} \cos\theta \cdot \sin\theta \, d\theta$$

$$= \frac{2\pi m}{ah^2} \cdot (h\nu - \chi) \cdot \epsilon^{-h\nu/kT} d\nu. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11')$$

Hence the number of electrons emitted per second per unit area by all frequencies of radiation higher than the threshold frequency $\nu_0 = \chi/h$ is

$$n = \frac{2\pi m}{ah^2} \cdot \int_{\chi/h}^{\infty} (h\nu - \chi) \, \epsilon^{-h\nu/kT} d\nu$$

$$= \frac{2\pi m}{ah^3} k^2 T^2 \int_{\chi/h}^{\infty} \left(\frac{h\nu - \chi}{kT}\right) \cdot \epsilon^{-h\nu/kT} \cdot \frac{h \, d\nu}{kT}$$

$$= \frac{2\pi m k^2}{ah^3} T^2 \cdot \epsilon^{-\chi/kT}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12')$$

Thus we arrive at practically the same law of thermionic emission as given in equation (18).

§ 5. *Summary and Discussion.*

In this paper the law of thermionic emission, in the form

$$I = \frac{2\pi mek^2}{h^3 K_2(T)} \cdot T^2 \cdot \epsilon^{-\chi/kT},$$

has been presented as a theorem in statistical mechanics. The function $K_2(T)$, which depends on the frequencies of metallic electrons, appears, from evidences of excess specific heat of metals over Dulong-Petit's value 3R, not to differ

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much from unity up to the melting-point of metals. It has next been shown on the basis of the theory of complete reversibility of physical processes that the emission law is the same if the mechanism be supposed to be radiative.

The arguments advanced in the deduction of this law are of quite general character. The apparatus of chemical constants and Nernst's Heat Theorem, by which one can get at this law on thermo-dynamic reasoning, is quite uncalled for in the present method. The assumptions adopted are :—

(1) The electrons inside the metals form space-lattices like the atoms in a crystal, and share in heat energy according to Planck's law of quanta.

(2) The external electrons are regarded as constituting an ideal monatomic gas, and are supposed to be emitted with Maxwell's law of distribution of velocities.

The idea of electronic lattices is not new. Such and similar ideas have already been adopted by Lindemann*, Haber †, Borelius ‡, and recently by Thomson § to explain electric and thermal conduction of metals and other metallic properties on the electron theory. The assumption with regard to the external electrons has been widely accepted. The recent experiments of Jones ‖ have proved conclusively that electrons are emitted from hot bodies with Maxwell's distribution of velocities.

It must, however, be noted that the law of emission considered here applies only to low concentrations of electrons emitted inside an ideal vacuum. In cases where the emission is profusely dense, the space-charge effect has got to be taken into consideration.

I have said nothing here about the nature of the work function χ, for I have discussed this point at some length in a previous paper¶. There I have pointed out that it is possible to evaluate χ from the constants of atomic space-lattices. The question of identity of photo-electric and thermionic work functions is probably uncertain. But the close correspondence between the two is unmistakable. Both are functions of the atomic volumes, and are much smaller than the ionization potentials of the elements in the vapour-phase. This shows that the closeness of atoms in the condensed state releases the force of restraint on the superficial

* Phil. Mag. xxix. p. 127 (1915).
† *Berl. Akad. Ber.* 1919, pp. 506, 990.
‡ *Ann. der Phys.* lvii. p. 278 (1918).
§ Phil. Mag. xliv. p. 657 (Oct. 1922).
‖ Proc. Roy. Soc. cii. pp. 734–751.
¶ Proc. Ind. Ass. Cult. Sc. ix. part 1, p. 4 (1924).

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electrons, so that the ionization potentials of the atoms in the condensed phase are lower than those of atoms in the vapour-phase.

In conclusion, I wish to thank Mr. R. H. Fowler for looking into the manuscript and for advancing helpful criticisms.

Note added in proof, June 11.—J. J. Weigle (Phys. Rev., Feb. 1925, p. 187) has recently presented us with very interesting calculations of the heat of evaporation of electrons from (1) the space-lattice constants and the coefficient of compressibility, and also from (2) the heat of evaporation of the metal, its ionizing energy, and the radii of the ions. The values so calculated agree well with each other and also with these determined from the thermionic emission data. This agreement is in further support of the idea of electron space-lattices in metal crystals.

XXVII. *The Laboratory Construction of Nernst Filaments.*

By Harry D. Griffith, *B.A., Carnegie Teaching Fellow in the University of Aberdeen* *.

THE author has been put to great inconvenience while conducting an investigation on short Infra-Red radiation through inability to obtain Nernst filaments. There is no source available as effective as these are in the region of the spectrum to be studied (up to 5μ), but they are not now obtainable commercially. No information on the old manufacturing process seems to have been published except for patent specifications which do not deal with the main difficulties. The working out of a method for making the filaments was a matter of some difficulty, and this paper is published in the hope that it may be of service to other investigators faced with a similar problem.

The construction of the filament itself is quite a different problem from the subsequent sealing-in of the electrodes, and is a far simpler matter. For the filament, the following mixture is suitable :—

Zirconium Oxide	80 per cent.
Thorium Oxide	10 ,,
Lime	5 ,,
Magnesium Oxide	5 ,,
Boric Acid	a trace

* Communicated by Prof. G. P. Thomson, M.A.

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This is ground very fine in an agate mortar, with glycerine or a solution of sugar, so as to yield a thick, creamy paste, which is then extruded into threads with a simple extrusion press with nozzle diameter 1·3 mm. and piston diameter 3 mm. The ratio between piston diameter and nozzle diameter should not be greater than this, and the paste must be worked until it is of a suitable consistency before extrusion. The threads are extruded onto a sheet-iron plate covered with a thin layer of magnesium oxide, and then left to dry. They are then heated slowly until the sugar chars, when they will be strong enough to be handled, and are cut into lengths of about 3 cm. These lengths are then passed through a small carbon arc taking about 3 amperes, after which they will be quite white, hard, and of the consistency of china.

Sealing-in the Electrodes.

The attachment of the negative electrode offers no difficulty. A fine platinum wire (diam. ·1 mm.) is bent into a loop, and slipped over one end of a piece of filament. The point of attachment is moistened with thorium nitrate solution, and covered with a layer of filament paste, diluted somewhat with thorium nitrate solution. The seal is slowly dried off in air till it is hard.

The positive seal gives more trouble, since during the running of the filament oxygen is evolved there, and this tends to force the platinum away from the paste, starting an arc which soon destroys the seal. The oxygen can be got away harmlessly through the presence in the seal of iron, manganese, or best yttrium. It is also necessary to have a considerable active area of platinum.

Five or six platinum wires diam. ·1 mm. are twisted together, and their ends arranged to clasp the filament as a jewel is held in its setting. The filament is inserted, the clasp damped with thorium nitrate solution, and then covered with a layer of a paste composed of equal parts of

Yttrium Oxide,
Thorium Oxide,
Cerium Oxide,
Zirconium Oxide,

made pasty with thorium nitrate solution.

The whole is dried out slowly in hot air, then ignited strongly to convert the nitrate to thoria, and is then ready for mounting. If both seals are made in this way, the

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filament would, presumably, work properly on alternating current. One end of the filament may be rigidly clamped, but the other should be attached only to a bent flexible wire (copper 40 S.W.G.), or the filament will be broken through expansion and contraction.

The Series Resistance.

Since the resistance of the filament decreases if the current through it increases, the circuit will be unstable without a suitable balancing resistance, which may consist of tungsten lamps. For a filament of diam. 1·3 mm., length 20 mm., two 60 watt 220 volt lamps in parallel are satisfactory. The current passing is then ·24 amp., and the pressure drop across the filament 96 volts.

The first time the filament is used it will be necessary to heat it and the seals red hot before it will conduct, but afterwards a much lower temperature suffices. Filaments made as described give a somewhat yellower light than the old commercial article, but if a whiter light is required it is probable that slight changes in the filament paste, such as the inclusion of cerium oxide, would have the desired effect.

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University of Aberdeen.

XXVIII. *The Theory of Molecular Interaction in the Liquid State.* *By* G. N. Antonoff, *D.Sc.* (*Manch.*) *.

Introduction.

When I began to work 25 years ago on liquid systems, the only theory that was then generally accepted was that of van der Waals, which can be described as a purely physical theory. There existed also the theory of De Heen, a kind of a chemical theory, but it did not receive general recognition, and can be regarded as practically abandoned. The same may be said about the theories of solutions. The predominant view ignored any interaction between either homogeneous or heterogeneous molecules. This view had many supporters and an extensive literature, together with a fair amount of quantitative relations which seemed to support the theory. On the other hand, the "chemical theory" (that of Mendeleieff and others) was

* Communicated by the Author.

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regarded for a long time merely as a suggestion having few followers and little or no quantitative relations capable of supporting it. However, in the course of time, a number of investigators * showed that the van der Waals theory, although giving a general picture fairly satisfactorily at first sight, did not show a sufficient agreement with the experimental data, and in this sense, in spite of its apparent success, the van der Waals formula cannot be regarded as an expression of a true law.

Although I was never a follower of either of these theories, I realized long ago that any theory which ignores altogether the interaction between the molecules cannot be of a comprehensive character.

In this paper I publish some evidence which enables one to formulate certain general laws which take into account the molecular state of the liquids. The theory here set forth formed itself in my mind as a result of my own experimental work, but at the present time advantage can be taken of quite different methods to corroborate my view.

In the first place such methods as the X-ray analysis throw light on the intimate structure of liquids; and particularly the statement made by Sir William H. Bragg in his lecture to the Chemical Society on "The Significance of Crystalline Structure" to the effect that "the ultimate unit of crystal structure or elementary parallelepiped is not the chemical molecule, but is a complex formed by the union of two, three, or four molecules"†.

The question arises whether the above unit remains the same when a crystal is melted and becomes a liquid, or whether it disintegrates into individual molecules. An attempt to answer this question can be found in the works of C. V. Raman (see 'Nature,' *ibid.*), who worked out special optical methods with the object of studying the intimate structure of liquids. The question cannot perhaps be regarded as definitely settled, but his evidence is in favour of the view that the above unit preserves its structure in the liquid state.

According to my theory it is necessary to assume that in some liquids, especially the associated liquids, the number of units in the molecule is sometimes more than four.

On the above assumption it becomes clear that the process of molecular disintegration between the melting-point and the critical point when the molecules become gaseous will be discontinuous, and will take place in several stages, for

* Young, Proc. Roy. Dublin Soc. xii. p. 374 (1910).
† See 'Nature,' cxi. p. 428.

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example, as follows:—

$$A_4 \rightleftarrows A_3 + A,$$

$$A_3 \rightleftarrows A_2 + A,$$

$$A_2 \rightleftarrows A_1 + A_1.$$

This scheme is in agreement with the facts described in the following pages.

The Theory.

The outlines of the theory described in my paper (Phil. Mag. xxxvi. p. 377, 1918) were originally applied to the systems liquid–liquid. In the above paper I have shown that the law connecting the surface tensions of the two liquid layers in equilibrium with the interfacial tension,

$$\alpha_{12} = \alpha_1 - \alpha_2,$$

where α_{12} is the interfacial tension and α_1 and α_2 are the surface tensions of both layers, implies the equality of molecular concentration of the two layers. This is a condition of equilibrium, and is supported not only by reasons purely mathematical, but also by the physico-chemical evidence.

As, however, the concentrations of the two layers are very different from one another, it is obvious that the liquids must consist of different kinds of molecules. The fact that the two layers have the same vapour-pressure and the same composition of vapour (Konovalov's law), I can only explain by assuming that the molecules forming the gaseous phase are uniformly distributed throughout the system. They thus have the same concentration in both liquid layers, and this concentration must be substantially identical with that of the gaseous phase. This is the only possible condition under which the so-called Konovalov's law can be interpreted physically.

Having observed during a long period the properties of the systems liquid–liquid *, I have always held the view that they are not only in many ways analogous to the systems liquid–gas, but that they are governed by similar physical laws.

I therefore apply without hesitation the just-exposed view to the systems liquid–gas. I assume that the process of formation of liquids is due to the formation of associated molecules, and that the molecules forming the gaseous phase penetrate the liquid phase without suffering any substantial change in concentration. In my recent paper

* *I. e.* systems consisting of two liquid layers.

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(published in *Zeit. Ph. Ch.* Bd. cxii. Heft 5/6, p. 461) I deduced an empirical law for the variation of δ with the temperature. It should be remembered that

$$\delta = \delta_l - \delta_v,$$

where δ_l = the density of the liquid,

δ_v = „ „ „ vapour.

From the above point of view the quantity δ has a definite physical meaning, and *represents the concentration of the associated molecules.* I assume that if there were no changes in the molecular state of liquids with change of temperature, a linear law ought to be expected as in gases.

$$\frac{d\delta}{dT} = K,$$

where T is the temperature reckoned from the critical point downwards. However, owing to the molecular association,

$$\frac{d\delta}{dT} = \frac{K \cdot dn}{dT},$$

where n is the number of associated molecules per unit volume. The law connecting n with the temperature must be of the form

$$\frac{dn}{dT} = \frac{K}{T+B}.$$

Thus

$$d\delta = \frac{K \cdot dT}{T+B}$$

$$= K \cdot d \ln (T+B),$$

$$\delta + c = K \cdot \ln (T+B),$$

which expression, by putting $K = \frac{1}{\lambda}$, can be represented in the form

$$Ae^{\lambda\delta} = T + B. \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

In the critical region it is essential that A = B; the equation then satisfies the condition $\delta = 0$ when T = 0. The expression (1), deduced on the above theory, is identical with the empirical expression on p. 462 of my previous paper (*loc. cit.*).

The experimental data show that the δ *curve* (see fig. 1, on which the figures for ethyl acetate are plotted) *is discontinuous in its character*, as will be shown later on, and

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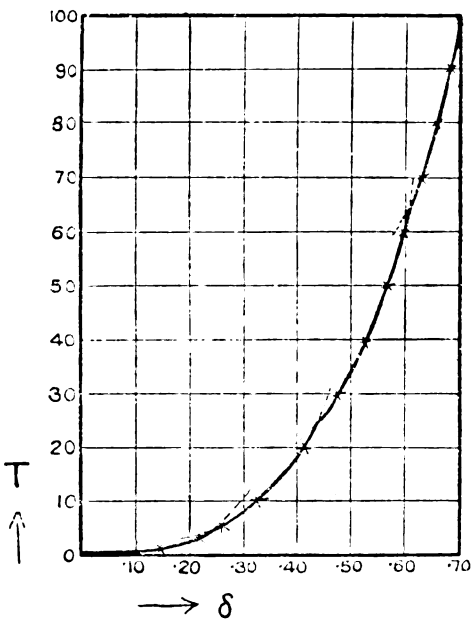
consists of portions, each satisfying the equation (1), with different constants for every subsequent portion. Thus, from the critical point downwards, the whole curve can be represented by a series of equations:

$$Ae^{\lambda\delta} = T + A,$$
$$A_1e^{\lambda_1\delta} = T + B_1,$$
$$A_2e^{\lambda_2\delta} = T + B_2,$$

and so on.

And this is a general law for all liquids.

Fig. 1.



It will be shown later on that a law of the same form holds true for the latent heats of evaporation, L:

$$Ce^{\mu L} = T + C,$$
$$C_1e^{\mu_1 L} = T + D_1,$$
$$C_2e^{\mu_2 L} = T + D_2, \text{ etc.},$$

where C, D, and μ are constants for a limited part of the curve between two kinks.

It has been suggested before that some sort of molecular clustering must take place in the liquid state (see Jeans, 'Dynamical Theory of Gases,' p. 203. The fact that the

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curve is discontinuous suggests the idea that the clustering or molecular association takes place according to Dalton's law of multiple proportions.

According to this theory all liquids must be regarded as associated, but they may differ in the nature and degree of association.

I am not in a position yet to formulate the difference between the normal and associated liquid exhaustively, but I think I am justified in making the following statement:—*Some liquids undergo* between their melting-point and the critical temperature *a greater number of the above changes than other liquids.* In other words, the continuous portions of the δ curve are shorter and more numerous. It may be that the corresponding states are connected with the number of the above changes.

Experimental Evidence.

In my previous paper I plotted δ's against the surface tension for benzene, and the curve obtained was distinctly discontinuous. I therefore assumed that it must be probably due, at least partially, to the discontinuity in the δ curve itself*. However, the discontinuity of the δ curve is not so obvious at first sight, even if the curve is drawn on a large scale, but the mathematical treatment which I have given is much more sensitive and demonstrates it quite clearly. Each portion of the δ curve can be represented in terms of an exponential function with a remarkable accuracy. If two exponential curves with different constants intersect in a given point, the discontinuity is beyond any doubt.

It is therefore necessary to consider whether the existing data are accurate enough to support my theory. This question, of course, is not easy to answer. As all my conclusions were based not on my own, but on other people's experiments, I felt that I was not myself in a position to form an opinion as to their accuracy. In the first instance I consulted on this subject Prof. J. Timmermans, of Brussels, as one experienced in carrying out precision measurements. As the question is a very delicate one, he advised me to write about it to Prof. Sydney Young, of Dublin, on whose experimental figures all my results are substantially based. Prof. Young was kind enough to give to this subject a very careful consideration, and I take the opportunity to express my best thanks to him. The nature of his answer is such that I could not form a definite opinion as to the accuracy of the results, the question being a very complicated one.

However, he indicates which figures he regards as most

* See also Dr. J. Geissler, *Zeit. f. Electrochemie*, Bd. xxiv. p. 101 (1918).

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reliable, and if I can prove the discontinuity for them I shall be on safer ground.

Thus he does not recommend me to rely on figures for benzene which were obtained nearly 30 years ago. With increased experience and improved methods the data for the paraffins, hexamethylene, and the esters, also acetic acid, are more accurate than the earlier data.

In view of the above, I had at first some difficulty in working out the experimental data.

However, in the course of time I found that some other properties also show discontinuity, confirming the existence of the kinks, always in the same ranges of temperature.

This enabled me to work out a number of cases from 0° C. up to the critical point, and to establish the number of changes within the above limits.

In the following section, evidence will be brought forward indicating that, apart from δ's, several other properties are discontinuous: viz.,

Densities of liquids (δ_l),
Densities of vapours (δ_v),
Latent heats of evaporation (L),
Viscosity (η),
Surface tensions (α).

On the Discontinuity of some Properties of Liquids.

It is very easy to show that the latent heats of evaporation, L, traced against the temperatures, show a marked discontinuity. The most sceptical mind cannot help noticing it simply by looking at the drawing, especially near the critical point. At low temperatures the curve sometimes flattens out and begins to approach a straight line, but on the whole the discontinuous character of the curve cannot inspire any doubts.

It is not so with densities. One can draw the densities on a large scale, and yet the discontinuity does not appear to be so obvious, especially at first sight.

It is easier to notice the same on δ curves than on either δ_l or δ_v curves, for reasons which will become clear later on.

I generally draw the δ curve against the temperature on a sufficiently large scale. By using a flexible steel curve I can detect the kinks in the regions of low temperatures with extreme ease. The curved part between two kinks can be fitted very easily and accurately into an exponential expression as (1).

At higher temperatures difficulties arise because of a greater curvature, owing to which interpolation becomes difficult, and sometimes involves much labour. This work can

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be greatly facilitated by observing the corresponding L curve (latent heat of evaporation), as both methods indicate, as a rule, the existence of kinks in the same intervals of temperature.

The following tables give the results obtained for three substances of a different chemical nature: viz., a hydrocarbon, an ester, and an alcohol, the figures being taken from the work of Prof. Young *.

In these tables T is the temperature reckoned from the critical point, t is the temperature from 0° C. In the column L the brackets show the position of kinks as indicated by the L (latent heat of evaporation) curve.

In these tables I give the values for δ, experimental and calculated by the exponential expression, which is generally given above each table in logarithmic form so as to enable the calculation of δ with the least expenditure of energy. In each table I extend the calculation on either side beyond the boundary within which the given law is valid. By two horizontal lines I separate the region within which the differences between the experimental and the calculated values are negligible. Outside it the differences begin to grow systematically as a rule, and their magnitude is often such that it is beyond the limits of experimental errors. Near the kinks the figures will be found sometimes between two horizontal lines. This indicates that the given point either fits into both intersecting curves, or its position is doubtful.

For each substance I also give the exponential equations, as such, tabulated together.

TABLE I.

Hexamethylene.

(1)

$$\log \delta = \log \{\log (T + 1000 \cdot 1) - 2 \cdot 82141\} - 1 \cdot 55470.$$

T.	t.	δ exp.	δ calc.	Diff.	L.
280	0	·7966	·7967	+ ·0001	
270	10	·7872	·7872		
260	20	·7776	·7777	+ ·0001	
250	30	·7680	·7680		
240	40	·7584	·7583	− ·0001	
230	50	·7485	·7485		
220	60	·7384	·7388	+ ·0004	
210	70	·7284	·7288	+ ·0004	
200	80	·7177	·7188	+ ·0011	
190	90	·7068	·7086	+ ·0018	

* *Loc. cit.*

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TABLE I. (*continued*).

(2)

$$\log \delta = \log\{\log(T+77{\cdot}31)-1{\cdot}39840\}-\bar{1}{\cdot}63000.$$

T.	t.	δ exp.	δ calc.	Diff.	L.
260	20	·7776	·7761	− ·0015	
250	30	·7680	·7672	− ·0008	
240	40	·7584	·7579	− ·0005	
230	50	·7485	·7483	− ·0002	
220	60	·7384	·7384		
210	70	·7284	·7283	− ·0001	
200	80	·7177	·7177		
190	90	·7068	·7067	− ·0001	
180	100	·6954	·6954		
170	110	·6835	·6835		
160	120	·6711	·6712	+ ·0001	
150	130	·65805	·6584	+ ·0004	
140	140	·6442	·6449	+ ·0007	
130	150	·62975	·6308	+ ·0010	

(3)

$$\log \delta = \log\{\log(T+52{\cdot}93)-1{\cdot}25990\}-{\cdot}20190.$$

200	80	·7177	·7181	+ ·0004	
190	90	·7068	·7071	+ ·0003	
180	100	·6954	·6955	+ ·0001	
170	110	·6835	·6836	+ ·0001	
160	120	·6711	·6711		}
150	130	·65805	·6581		}
140	140	·6442	·6442		}
130	150	·62975	·6297		}
120	160	·6143	·6143		}
110	170	·5981	·5981		}
100	180	·5805	·5809	+ ·0004	
90	190	·5612	·5623	+ ·0011	
80	200	·5406	·5426	+ ·0020	
70	210	·5183	·5213	+ ·0030	
60	220	·4931	·4981	+ ·0050	
50	230	·4646	·4728	+ ·0082	

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TABLE I. (*continued*).

(4)

$$\log \delta = \log\{\log (T+18{\cdot}71)-{\cdot}88034\}-{\cdot}31381.$$

T.	*t*.	δ exp.	δ calc.	Diff.	L.
130	150	·6297	·6273	− ·0020	
120	160	·6143	·6126	− ·0017	
110	170	·5981	·5969	− ·0012	
100	180	·5805	·5498	− ·0007	
90	190	·5612	·5612		
80	200	·5406	·5407	+ ·0001	
70	210	·5183	·5183		
60	220	·4931	·4931		
50	230	·4646	·4645	− ·0001	
40	240	·4313	·4313		
30	250	·3914	·3919	+ ·0005	
20	260	·3422	·3435	+ ·0013	
15	265	·3106	·3144	+ ·0038	
10	270	·2692	·2805	+ ·0113	
6	274	·2257	·2489	+ ·0232	

(5)

$$\log \delta = \log\{\log (T+5{\cdot}20)-{\cdot}3670\}-{\cdot}4804.$$

40	240	·4313	·4261	− ·0052	
30	250	·3914	·3904	− ·0010	
20	260	·3422	·3422		
15	265	·3106	·3105	− ·0001	
10	270	·2692	·2695	+ ·0003	
6	274	·2257	·2257		
3	277	·1787	·1809	+ ·0022	
1	279	·1288	·1407	+ ·0119	

(6)

$$\log \delta = \log\{\log(T+{\cdot}0727)-\bar{2}{\cdot}8615\}-{\cdot}9590.$$

6	274	·2257	·2113	− ·0144	
3	277	·1787	·1787		
1	279	·1288	·1285	− ·0003	
0	280	0	0		

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Formulæ.

(1) $66{\cdot}30e^{{\cdot}8258\delta}=\mathrm{T}+1000{\cdot}1.$
(2) $25{\cdot}03e^{3{\cdot}351\delta}=\mathrm{T}+77{\cdot}31.$
(3) $18{\cdot}20e^{3{\cdot}665\delta}=\mathrm{T}+52{\cdot}93.$
(4) $7{\cdot}591e^{4{\cdot}743\delta}=\mathrm{T}+18{\cdot}71.$
(5) $2{\cdot}328e^{6{\cdot}961\delta}=\mathrm{T}+5{\cdot}20.$
(6) $\cdot0727e^{20{\cdot}97\delta}=\mathrm{T}+\cdot0727.$

Table II.

Ethyl acetate.

(1)

$$\log\delta=\log\{\log(\mathrm{T}+459{\cdot}65)-2{\cdot}37501\}-\bar{1}{\cdot}71189.$$

T.	*t*.	δ exp.	δ calc.	Diff.	L.
250·1	0	·9243	·9243		
240·1	10	·9125	·9123	−·0002	
230·1	20	·9002	·9003	+·0001	
220·1	30	·8880	·8880		
210·1	40	·8754	·8754		
200·1	50	·8624	·8627	+·0003	
190·1	60	·8490	·8498	+·0008	
180·1	70	·8350	·8367	+·0017	
170·1	80	·8210	·8234	+·0024	

(2)

$$\log\delta=\log\{\log(\mathrm{T}+228{\cdot}31)-1{\cdot}87511\}-\bar{1}{\cdot}88169.$$

250·1	0	·9243	·9253	+·0010	
240·1	10	·9125	·9133	+·0008	
230·1	20	·9002	·9010	+·0008	
220·1	30	·8880	·8884	+·0004	
210·1	40	·8754	·8756	+·0002	
200·1	50	·8624	·8624		
190·1	60	·8490	·8489	−·0001	
180·1	70	·8350	·8352	+·0002	
170·1	80	·8210	·8210		
160·1	90	·8065	·8065		
150·1	100	·7910	·7916	−·0006	
140·1	110	·7751	·7763	+·0010	
130·1	120	·7580	·7607	+·0027	
120·1	130	·7402	·7445	+·0043	

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TABLE II. (*continued*).

(3)

$$\log \delta = \log \{\log (T + 62{\cdot}72) - 1{\cdot}30211\} - {\cdot}11289.$$

T.	*t*.	δ exp.	δ calc.	Diff.	L.
200·1	50	·8624	·8618	−·0006	
190·1	60	·8490	·8487	−·0003	
180·1	70	·8350	·8352	+·0002	
170·1	80	·8210	·8211	+·0001	
160·1	90	·8065	·8065		
150·1	100	·7910	·7910		
140·1	110	·7751	·7750	−·0001	
130·1	120	·7580	·7580		
120·1	130	·7402	·7402		
110·1	140	·7213	·7213		
100·1	150	·7003	·7014	+·0011	
90·1	160	·6775	·6802	+·0027	
80·1	170	·6531	·6575	+·0044	
70·1	180	·6265	6332	+·0067	

(4)

$$\log \delta = \log \{\log (T + 37{\cdot}64) - 1{\cdot}12678\} - {\cdot}16002.$$

140·1	110	·7751	·7770	+·0019	
130·1	120	·7580	·7595	+·0015	
120·1	130	·7402	·7410	+·0008	
110·1	140	·7213	·7213		
100·1	150	·7003	·7003		
90·1	160	·6775	·6776	+·0001	
80·1	170	·6531	·6531		
70·1	180	·6265	·6265		
60·1	190	·5966	·5972	+·0006	
50·1	200	·5630	·5648	+·0018	
40·1	210	·5231	·5284	+·0052	
30·1	220	·4757	·4871	+·0114	

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TABLE II. *(continued).*

(5)

$$\log \delta = \log \{\log (T + 12{\cdot}80) - {\cdot}7329\} - {\cdot}2773.$$

T.	*t.*	δ exp.	δ calc.	Diff.	L.
90·1	160	·6775	·6756	−·0019	
80·1	170	·6531	·6522	−·0009	
70·1	180	·6265	·6266	+·0001	
60·1	190	·5966	·5966		
50·1	200	·5630	·5628	−·0002	
40·1	210	·5231	·5231		
30·1	220	·4757	·4750	−·0007	
20·1	230	·4150	·4142	−·0008	
10·1	240	·3279	·3311	+·0032	

(6)

$$\log \delta = \log \{\log (T + 5{\cdot}60) - {\cdot}3915\} - {\cdot}3898.$$

40·1	210	·5231	·5170	−·0061	
30·1	220	·4757	·4733	−·0024	
20·1	230	·4150	·4150		
10·1	240	·3279	·3279		
5·1	246	·2599	·2599		
3·1	247	·2199	·2234	+·0035	
1·1	249	·1551	·1771	+·0220	

(7)

$$\log \delta = \log \{\log (T + {\cdot}120) - \bar{1}{\cdot}0792\} - {\cdot}8127.$$

10·1	240	·3279	·2971	−·0308	
5·1	245	·2599	·2522	−·0077	
3·1	247	·2199	·2199		
1·1	249	·1551	·1550	−·0001	
0	250·1	0	0		

Formulæ :

(1) $237{\cdot}1e^{1{\cdot}186\delta} = T + 459{\cdot}65.$

(2) $94{\cdot}43e^{1{\cdot}754\delta} = T + 228{\cdot}31.$

(3) $20{\cdot}05e^{2{\cdot}986\delta} = T + 62{\cdot}72.$

(4) $13{\cdot}39e^{3{\cdot}328\delta} = T + 37{\cdot}64.$

(5) $5{\cdot}406e^{4{\cdot}360\delta} = T + 12{\cdot}80.$

(6) $2{\cdot}463e^{5{\cdot}649\delta} = T + 5{\cdot}60.$

(7) $\cdot 120e^{14{\cdot}96\delta} = T + {\cdot}120.$

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Table III.

Propyl alcohol.

(1)

$$\log \delta = \log \{\log (T - 99{\cdot}60) - 2{\cdot}96080\} - {\cdot}39980.$$

T.	*t.*	δ exp.	δ calc.	Diff.	L.
263·7	0	·8193	·8179	−·0014	
253·7	10	·8110	·8110		
243·7	20	·8034	·8037	+·0003	
233·7	30	·7959	·7959		
223·7	40	·7873	·7874	−·0001	
213·7	50	·7782	·7782		
203·7	60	·7696	·7574	−·0122	
193·7	70	·7604	·7449	−·0155	
183·7	80	·7510	·7310	−·0200	
173·7	90	·7409	·7152	−·0257	

(2)

$$\log \delta = \log \{\log (T - 1{\cdot}30) - {\cdot}43840\} - {\cdot}38505.$$

243·7	20	·8034	·8019	−·0015	
233·7	30	·7959	·7943	−·0016	
223·7	40	·7873	·7865	−·0008	
213·7	50	·7782	·7782		
203·7	60	·7696	·7696		
193·7	70	·7604	·7605	+·0001	
183·7	80	·7510	·7510		
173·7	90	·7409	·7410	+·0001	
163·7	100	·7302	·7302		
153·7	110	·7188	·71885		
143·7	120	·7066	·7067	+·0001	
133·7	130	·6934	·6937	+·0003	
123·7	140	·6794	·6796	+·0002	
113·7	150	·6634	·6644	+·0010	

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TABLE III. (*continued.*)

(3)

$$\log \delta = \log\{\log (T-47{\cdot}40)-\bar{1}{\cdot}2893\}-{\cdot}5817.$$

T.	*t.*	δ exp.	δ calc.	Diff.	L.
163·7	100	·7302	·7275	−·0027	
153·7	110	·7188	·7171	−·0017	
143·7	120	·7066	·7060	−·0006	
133·7	130	·6934	·6934		
123·7	140	·6794	·6794		
113·7	150	·6634	·6634		
107·7	160	·6462	·6449	−·0013	
93·7	170	·6273	·6226	−·0047	
83·7	180	·6060	·5948	−·0112	

(4)

$$\log \delta = \log \{\log(T+34{\cdot}30)-1{\cdot}0763\}-{\cdot}2157.$$

123·7	140	·6794	·6830	+·0036
113·7	150	·6634	·6657	+·0023
103·7	160	·6462	·6473	+·0011
93·7	170	·6273	·6273	
83·7	180	·6060	·6059	−·0001
73·7	190	·6828	·5825	−·0003
63·7	200	·6567	·5568	+·0001
53·7	210	·527	·5283	+·0010
43·7	220	·492	·4965	+·0036

(5)

$$\log \delta = \log \{\log (T+12{\cdot}33)-{\cdot}7126\}-{\cdot}3225.$$

73·7	190	·5828	·5806	−·0022
63·7	200	·5567	·5551	−·0016
53·7	210	·5273	·5269	−·0004
43·7	220	·4929	·4929	
33·7	230	·4526	·4523	−·0003
23·7	240	·4016	·4017	+·0001
13·7	250	·3345	·3345	
3·7	260	·2295	·2348	+·0053

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TABLE III. (*continued*).

(6) Figures not available.

Formulæ.

(1) $\cdot 09137e^{9\cdot 162\delta}=\mathrm{T}-99\cdot 60.$	(4) $11\cdot 90e^{3\cdot 787\delta}=\mathrm{T}+34\cdot 30.$
(2) $2\cdot 744e^{5\cdot 588\delta}=\mathrm{T}-1\cdot 30.$	(5) $5\cdot 160e^{4\cdot 838\delta}=\mathrm{T}+12\cdot 33.$
(3) $\cdot 1947e^{8\cdot 788\delta}=\mathrm{T}-47\cdot 40.$	(6) $\mathrm{A}e^{\lambda\delta}=\mathrm{T}+\mathrm{A}.$

A look at these equations, as well as at the above tables, indicates that these kinks are general for all regions. Although in some individual cases the figures may be doubtful, I think the number of cases where there can be no doubt at all is sufficiently large to allow us to regard the fact as established.

It should be added that I have had experience with a large number of liquids, using figures of different authors, and everywhere the result is the same.

I shall now proceed to show that the δ_l and δ_v curves are discontinuous as well. This is not so easy to show, because in this case the discontinuity is not quite so pronounced as in the case of δ curves.

However, it can be shown by the following method :—

To solve the equation

$$\ddot{\delta}=\delta_l-\delta_v=\frac{\log\left(\frac{\mathrm{T}+\mathrm{B}}{\mathrm{A}}\right)}{\cdot 4343\lambda}. \quad . \quad . \quad . \quad . \quad (2)$$

for δ_l and δ_v respectively it is necessary to have another equation connecting the above quantities with the T. To this end, advantage can be taken of the Cailletet-Mathias law of rectilinear diameter in the cases where this law is valid.

According to this law

$$\frac{\delta_l+\delta_v}{2}=\frac{\mathrm{T}+b}{a}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where a and b are constants, *i. e.* it is a rectilinear function of temperature.

Or using for the sake of simplicity the symbol Δ for $\frac{\delta_l-\delta_v}{2}$,

$$\Delta=\frac{\mathrm{T}+b}{a}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The question is whether this law is general and accurate enough. A more close examination shows that probably it is not. But for the purposes of this investigation it can easily be assumed that a and b remain constant within a given portion of the curve for which A, B, and λ are constant. I thus assume that a and b also undergo sudden

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changes from time to time, although their change is minute compared with the corresponding change in A, B, and λ.

Thus for a given interval δ_l and δ_v can be evaluated from the equations (2) and (3) or (4):

$$\delta_l = \Delta + \tfrac{1}{2}\,\frac{\log\left(\frac{T+B}{A}\right)}{\cdot 4343\,\lambda}, \quad . \quad . \quad . \quad . \quad (5)$$

$$\delta_v = \Delta - \tfrac{1}{2}\,\frac{\log\left(\frac{T+B}{A}\right)}{\cdot 4343\,\lambda}. \quad . \quad . \quad . \quad . \quad (6)$$

The two expressions differ only in so far as the logarithmic term containing A, B, and λ comes in with the opposite sign. As these constants undergo sudden changes at regular intervals, the discontinuity of both curves is thereby accounted for.

In the expression $\delta_l + \delta_v$ the discontinuity is substantially compensated, at least the part of it due to the change in the constants A, B, and λ, because the logarithmic term disappears.

On the other hand, in the expression $\delta_l - \delta_v$ the two halves of the logarithmic expression add up, and the discontinuity is of a much more pronounced character.

For example, I calculated $\Delta \pm \frac{1}{2}\delta$, which is the accurate expression for δ_l and δ_v respectively, for two different intervals of temperature, using the following expressions:

For 220—170 T

$$\frac{T+594\cdot 91}{2197\cdot 7} \pm \tfrac{1}{2}\,\frac{\log\,(T+77\cdot 31)-1\cdot 39840}{1\cdot 45546}, \quad . \quad (7)$$

and for 160—110 T

$$\frac{T+603\cdot 35}{2222\cdot 3} \pm \tfrac{1}{2}\,\frac{\log\,(T+52\cdot 93)-1\cdot 25988)}{1\cdot 59191}. \quad . \quad (8)$$

The results are given in Table IV.

By prolonging the calculations by the above formulæ, one can also observe a systematic deviation. In cases represented in Tables I., II., and III. the differences are magnified owing to the addition of two effects, *i. e.* of two logarithmic terms.

In the curves δ_l and δ_v the same deviations ought to be about half as big, if the effect were due to the half-logarithmic term with constants A, B, and λ only.

It appears, however, that there is also a small change in constants a and b; at least it seems to be so in the case of hexamethylene.

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TABLE IV.

T.	Δ exp.	Δ calc.	½δ calc.	δ_l exp.	δ_l calc.	δ_v exp.	δ_v calc.
220	·3708	·3708	·3692	·7400	·7400	·0016	·0016
210	·3664	·3663	·3642	·7306	·7305	·0022	·0021
200	·3617	·3617	·35885	·7205	·7206	·0029	·0028
190	·3572	·3571	·3534	·7106	·7105	·0038	·0037
180	·3526	·3526	·3477	·7003	·7003	·0049	·0049
170	·3481	·3480	·34175	·6898	·6898	·0063	·0062
160	·3435	·3435	·33555	·6791	·67905	·00796	·00795
150	·3390	·3390	·32905	·6680	·66805	·00995	·00995
140	·3344	·3345	·3221	·6565	·6566	·01227	·01210
130	·3299	·3300	·31485	·6448	·64485	·01505	·01515
120	·3254	·3255	·30715	·6325	·63265	·01818	·01835
110	·3210	·3210	·29905	·6200	·62005	·02193	·02195

The above relations assume the validity of Mathias-Cailletet's law. In cases when it is not valid, it is sometimes possible to see the discontinuity of the δ_l and δ_v curves simply by drawing the curves on a sufficiently large scale: for example, for propyl alcohol the law of rectilinear diameter does not hold true. However, the discontinuity of the densities is so sharp in the region between 60° and 50° C. that it cannot remain unnoticed.

Latent Heats of Evaporation.

The discontinuous character of the mechanism of disaggregation of liquids is particularly well demonstrated by the latent heats of evaporation (L).

Plotting the L's against the temperature T, one can see that the curve consists of curved portions intersecting with each other within the same ranges of temperature as in the δ curves. The bits of the curve are generally strongly curved at higher temperatures, especially near the critical point. Although the work near the critical point may be difficult, and involve considerable experimental errors, the angle at which the curves intersect with one another is such that the existence of the kinks is beyond any doubt.

The variation of L with temperature can be expressed fairly well by the expression of the same type as (1), viz.

$$Ce^{\mu L} = T + D,$$

where C, μ, and D are constants for the given interval of the curve.

At lower temperatures the curves often flatten out, and sometimes begin to approach a straight line.

In the following table the results are given for propyl alcohol.

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TABLE V.

Propyl alcohol.

L Curves.

(2)

$\log L = \log\{\log(T-62{\cdot}70)-{\cdot}5785\}-\bar{3}{\cdot}9393.$				
T.	*t.*	L exp.	L calc.	Diff.
183·7	80	173	173	
173·7	90	169	168·7	−0·3
163·7	100	164	164	
153·7	110	159	158·8	−0·2
143·7	120	153	153	

(3)

$\log L = \log\{\log(T-100{\cdot}2)-\bar{4}{\cdot}5659\}-\bar{2}{\cdot}5281.$				
133·7	130	147	147	
123·7	140	142·4	142·4	
113·7	150	135·3	135·3	

(4)

$\log L = \log\{\log(T+156{\cdot}05)-2{\cdot}0601\}-\bar{3}{\cdot}4390.$				
103·7	160	129	129	
93·7	170	122·8	122·7	−0·1
83·7	180	116·3	116·3	
73·7	190	109·6	109·6	
63·7	200	102·2	102·5	+0·3

(5)

$\log L = \log\{(\log T+58{\cdot}04)-1{\cdot}6353\}-\bar{3}{\cdot}6401.$				
53·7	210	94·5	94·56	+0·06
43·7	220	85·3	85·25	−0·05
33·7	230	75·0	74·97	−0·03
23·7	240	63·4	63·46	+0·06
13·7	250	50·6	50·50	−0·10

Formulæ :

(2) $3{\cdot}789e^{{\cdot}02007L}=T-62{\cdot}70.$ | (4) $114{\cdot}2e^{{\cdot}00633L}=T+155{\cdot}04.$

(3) $\cdot00037e^{{\cdot}07767L}=T-100{\cdot}2.$ | (5) $43{\cdot}22e^{{\cdot}01005L}=T+58{\cdot}04.$

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Surface Tensions.

The discontinuity is still more pronounced if the δ's are plotted against the surface tensions; but nothing more definite can be said about it until the true law connecting the surface tensions and the densities is known.

Apart from the above, I have also come to the conclusion that the surface tensions plotted against the temperature show also signs of discontinuity. Although at first sight it appears to be a linear function of temperature, a more close examination shows that this is not the case at all. From a logarithmic plot it may appear that an expression may hold true of the type—

$$\alpha = (kT)_n,$$

where α is the surface tension and k and n constants.

However, the examination of errors makes me believe that such a law can be only regarded as a rough approximation, and it certainly is not the true law.

I have come to the conclusion that an accurate law can only be found for a limited part of the curve. The experimental data show that also in this case the law can be expressed by means of an exponential formula. If we plot the surface tensions (α) as abscissæ, and the temperatures (T) as ordinates, the relation will be of the form

$$\alpha + B = Ae^{\lambda T}.$$

Thus for ethyl acetate in the interval of temperatures 150·1—110·1 T the above formula acquires the form

$$\alpha + 33{\cdot}62 = 33{\cdot}19e^{{\cdot}0024T},$$

and in the interval 100·1—70·1 T

$$\alpha + 21{\cdot}32 = 20{\cdot}93e^{{\cdot}0035T}.$$

The figures for the above expressions are taken from the work of Ramsay and Shields (Phil. Trans. clxxxiv. I, p. 647, 1893). They indicate the presence of kinks in the same interval of temperatures as other properties do. They also indicate that near the critical point the surface tension will follow very closely the vertical axis, *i. e.* the increase of α with temperature will be only minute at first.

Viscosities.

It is generally assumed that the association of liquids must be intimately connected with their viscosities. It is therefore probable that if the association takes place in stages,

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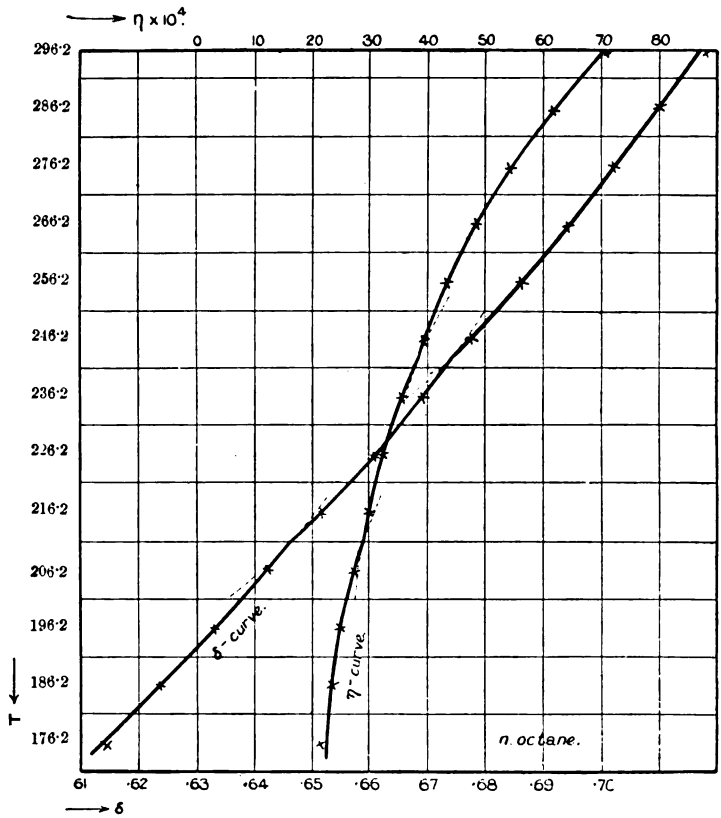
as indicated above, the viscosity-temperature curve will be also discontinuous. The existing data, although not very complete, throw enough light on the subject to make it clear that such is actually the case. Fig. 2 represents a δ curve, together with a corresponding viscosity curve (η curve) plotted against temperatures T (vertical axis

Fig. 2.



common to both curves) for *n*-octane. The viscosities ($\eta \times 10^4$) are plotted on the upper horizontal axis. On the lower axis the values of δ are plotted. The values of δ are taken from Sydney Young (*loc. cit.*) and the viscosities from the Landolt-Börnstein Tables. The figure shows that both curves are discontinuous, and the kinks on both curves correspond to more or less the same intervals of temperature.

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It can also be observed from fig. 2 that the form of law will be the same as for surface tensions, viz.

$$\eta + C = De^{\mu T}.$$

In fig. 2 the viscosities of a liquid were plotted against the temperature. More strictly one ought to plot

$$\eta = \eta_l - \eta_v,$$

where η_l is the viscosity of the liquid and η_v that of its vapour. However, at low temperatures η_v is small, and η_l can be readily used as a good approximation for η. One can thus find that the law is of the form as indicated.

Conclusion.

The view that liquids contain more than one kind of molecules is not novel. Such a view has already been expressed in a paper by C. Drucker *, and also in the works of A. Smits †, although the latter author chiefly deals with such substances as sulphur and phosphorus, which liquids may not be regarded as typical (see also Cohen ‡ and others).

This paper is intended to demonstrate the discontinuity of certain properties of liquids—viz., of the densities of the vapour, the densities of the liquid, of the latent heats of evaporation, the surface tensions, and viscosities.

The observation of the results tabulated in the accompanying tables shows that the mechanism of disintegration of the liquids proceeds always according to a definite and general law. In this sense there is no difference in the behaviour of the so-called "associated" and "normal" liquids. However, the examination of the constants of the exponential equations reveals some peculiarity in the case of an "associated" liquid, propyl alcohol. Whereas in the case of ethyl acetate and hexamethylene the numerical values of the constants vary in a certain more or less regular manner (for example, the constant B increases as we proceed from the critical point, and the constant λ on the contrary diminishes), their variation is most peculiar in the case of propyl alcohol. So the constant B increases at first as in the case of "normal" liquids, and then even changes sign. Also the constants λ and A show a peculiar behaviour.

It is noteworthy that the equations for the latent heat of evaporation (L) are not only of the same form, but they show

* *Zeit. Phys. Ch.* lxviii. p. 616 (1909).

† *Zeit. Phys. Ch.* lxxvi, p. 421 (1911); lxxvii. p. 367 (1911).

‡ See numerous papers in *Zeit. Phys. Ch.* and elsewhere.

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the same peculiarities, viz. the constants B also increase at first, change sign, and so on.

Thus it looks as if L was intimately related to δ. Both properties are discontinuous and show kinks in the same places, and they both become $=0$ at the critical point. All this can receive a reasonable explanation if the association of molecules takes place according to the law of multiple proportion. It would then be quite natural to expect a more radical change near the critical point. For example, if a change

$$A_1 + A_1 \rightleftarrows A_2$$

is taking place, and is succeeded by a change, say

$$A_2 + A_1 \rightleftarrows A_3,$$

the kinks will be well pronounced. On the other hand, in a change, say

$$A_{10} + A_1 \rightleftarrows A_{11},$$

the addition of A_1 to an already complicated molecule will produce an effect which may be hardly noticeable at all.

The examples worked out in this paper indicate on the whole that such is actually the case, and the kinks, being well pronounced near the critical point, become less and less noticeable at lower temperatures (see fig. 1). It can be seen that the increase of δ per change diminishes as we proceed from the critical point, viz. its values are ·25, ·20, ·15, ·10, etc.

However, in some cases at low temperatures the kinks may become of such a nature as to indicate a deeper change.

In this paper I regard the vapour as the dissociation product, and in the above schemes it figures as one of the reacting bodies. Such a view accounts for the discontinuity of the density of the vapour.

However, at lower temperatures the vapour becomes negligible, and yet the δ curve may sometimes indicate a substantial change.

Considerations of that kind make me believe that at lower temperatures some other change may take place. For example, it seems natural to conclude that only the first three changes from the critical point in the case of propyl alcohol proceed "normally," as I may call it. The other three changes suggest something different, and particularly the last one (numbered (1) in the tables). In the latter case

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a more substantial change suggests itself. For example,

$$A_n + A_n \ldots \rightleftarrows A_{nn},$$

or something of that kind.

The fact that in the latter case the curve can be expressed by a formula of the same form as above makes me believe that in this case also a chemical change must be at the bottom of it.

Apart from the scheme just indicated, I can also think of such a change as will consist in an intermolecular re-grouping, in which case the form of the δ curve may remain substantially the same.

However, I can quite believe that in the vicinity of the melting-point the above relations may cease to hold true. Such is, for example, the case with water at about 4° C.

The explanation of this case can be found in Tyndall's work, 'Heat a Mode of Motion,' 1908, p. 108, where a model is given explaining the behaviour of water at about 4° C. In such a case the molecules are assumed to be in such a proximity to one another that the friction becomes an important factor in accounting for the above phenomenon.

It was mentioned in the Introduction that there is some evidence of association in the liquid state (Sir Wm. Bragg, C. V. Raman), suggesting that near the melting-point the molecular unit consists of 2, 3, 4, or more molecules.

On the other hand, in a gaseous state the molecular weight is known to correspond to a simple molecule (at least in cases dealt with in this paper).

The question arises, where does the association take place? It is highly improbable that it should take place directly below the critical point, or that it should take place suddenly somewhere else between the critical point and the melting-point.

However, the facts set out in this paper suggest that it takes place in several stages, and I do not think the kinks here described can have any other interpretation than that it takes place in accordance with the law of multiple proportions.

Summary.

1. In this paper evidence has been collected to show that the temperature changes in the liquid state take place in a discontinuous manner.

2. Four properties have been investigated in this paper—viz. densities, latent heats of evaporation, surface tensions, and viscosities.

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3. They all show kinks at the same temperatures.

4. The densities (δ) and latent heats of evaporation (L) vary with temperature according to a definite exponential law which is general for both normal and associated liquids and practically for all ranges of temperature, viz.

$$Ae^{\lambda\delta}=T+B \quad \text{and} \quad Ce^{\mu L}=T+D,$$

where T is the temperature reckoned from the critical point. These formulæ are valid for an interval between two kinks with given constants. For each interval the constants are different, but the form of law remains the same. The curve, plotted as in fig. 1, is convex towards the horizontal axis.

5. The surface tensions (α) and viscosities (η) similarly follow a simple and also an exponential law, viz.

$$\alpha+B=Ae^{\lambda T} \quad \text{and} \quad \eta+C=De^{\mu T}.$$

Both expressions are such that not the properties (α, η) but T is in the exponential. The curve is concave towards the horizontal axis.

6. The above evidence indicates that the discontinuity is an intrinsic property of liquids, and is interpreted as an indication of definite molecular changes in given intervals of temperature.

XXIX. *The Atomic Structure Factor in the Intensity of Reflexion of X-Rays by Crystals.* By D. R. Hartree, *M.A., Fellow of St. John's College, Cambridge* *.

§ 1. *Introduction.*

THE intensity of reflexion of X-rays by a crystal depends on several variables, one of which is the nature of the atoms composing it; the effect of this variable is represented in the formula for the intensity of reflexion † by the introduction of the number F for each atom, which represents the ratio of the amplitude of the wave scattered by this atom to the amplitude of the wave scattered by an electron. Adopting the classical theory, which at least gives results

* Communicated by Prof. W. L. Bragg, F.R.S.

† See W. H. and W. L. Bragg, 'X-Rays and Crystal Structure,' 4th edition, p. 203 *et seqq.*, where references to the original theoretical work of C. G. Darwin and A. H. Compton are given. See also W. L. Bragg, R. W. James, and C. H. Bosanquet, Phil. Mag. xli. p. 309; xlii. p. 1 (1921); xliv. p. 433 (1922).

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of the right order of magnitude *, it is clear that F must depend not only on the atom, but also on the angle of scattering, *i.e.* on the glancing angle, and on the wave-length of the incident radiation; for, if the wavelets scattered by all the electrons were in phase, F would be equal to the number of electrons concerned in the scattering, but if the differences of phase between the wavelets scattered by different electrons were appreciable, the amplitude of the wave scattered by the atom as a whole would be less than it would be if the wavelets were in phase, so that F is less than the number of electrons concerned in the scattering; these phase differences vary, and so F varies, with the glancing angle and wave-length.

The dependence of F on glancing angle and wave-length depends on the dimensions of the atomic orbits, and on the distribution of electrons in them. Approximate dimensions of the core orbits of some atoms can be found from the results of a numerical analysis of the terms of the optical and X-ray spectra, and the dimensions of orbits of other atoms interpolated from them, so that it is possible to calculate approximate values of F as a function of the glancing angle for any atom; these values can be represented by a graph which may be called an "F-curve." These F-curves may be of value in the analysis of crystal structure by X-rays, as will be explained shortly; the object of this paper is to give data from which the approximate F-curve for any ion may be constructed very simply, and to give F-curves for some interesting ions.

The importance of F-curves for the X-ray analysis of crystal structure can be explained shortly as follows.

For the simplest crystal structures (*e.g.* the elements crystallizing in the cubic system, or salts of the NaCl type), in which the positions of all atoms are given by considerations of symmetry once the general scheme or space group of the arrangement is known from X-ray results, the analysis does not depend on the F-curves for the atoms of the crystal; and for structures in which the positions of most of the atoms can be determined from considerations of symmetry alone, but which involve one parameter (*e.g.* the calcite series), or perhaps two, the values of these parameters can often be determined very closely from the abnormally low or high intensities of a few orders of reflexion from a small number of faces, without reference to the relative scattering powers of different atoms. But for more complicated structures, in

* *Cf.* W. L. Bragg, R. W. James, and C. H. Bosanquet, *loc. cit.* (3rd paper, p. 446).

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which the positions of few or none of the atoms are given by considerations of symmetry and the number of parameters is large, it becomes necessary to make more use of the intensities of reflexion of different orders and from different faces, and in order to do this fully it is necessary to know something about the relative amplitudes of the waves scattered by different atoms at different glancing angles *.

Though the method of calculating F-curves given in this paper involves some approximation and doubtful assumptions, it is hoped that the results obtained may form a better basis for X-ray analysis than the assumption usually, if not always, made hitherto, that the amplitude of the wave scattered by an atom is proportional to its atomic number.

§ 2. *General Theory of the Method.*

It will be assumed that, for the purpose of calculating the intensity of reflexion from a crystal as a whole, the total effect of all the atoms of one kind, situated at corresponding points of different elementary cells of the space-lattice, can be treated as if each atom consisted of a spherically symmetrical distribution of scattering material †.

For reflexion of X-rays of wave-length λ at glancing angle β, the contribution to the value of F from an electron in a circular core orbit ‡ of radius r is $\xi^{-1}\sin\xi$, where

$$\xi = (4\pi r \sin\beta)/\lambda. \quad . \quad . \quad . \quad . \quad . \quad (2\cdot1)$$

If the electron in a non-circular core orbit spends a fraction df of a radial period between radii r and $r+dr$, the contribution from this orbit to F is $\oint \xi^{-1}\sin\xi\, df$, so that the total value of F is

$$F = \Sigma \oint \xi^{-1}\sin\xi\, df, \quad . \quad . \quad . \quad . \quad (2\cdot2)$$

the summation being taken over all core orbits.

Thus if df/dr is known as a function of r for the core orbits of an atom, F can be calculated. For approximate evaluation of F the work can be much simplified; the results

* A further discussion and illustration of the use of F-curves in crystal analysis is given in a note by Prof. W. L. Bragg accompanying this paper.

† For a further discussion of this assumption, see a previous paper by the present writer, Phil. Mag. xlvi. p. 1091 (1923), especially § 4.

‡ See Bragg, James, and Bosanquet, *loc. cit.* (3rd paper, p. 439), and D. R. Hartree, Phil. Mag. (*loc. cit.* § 2).

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of numerical calculation of core orbits show that the progress of time in all non-circular core orbits is very similar; more precisely, the fraction of a radial period which an electron spends between any given fractions of the maximum radius of the orbit is very nearly the same for all such orbits, so that if r_0 is the maximum radius and $r/r_0 = r'$, df/dr' is very nearly the same function of r' for them all (see § 3). If we neglect the small differences of df/dr' as a function of r' for different orbits, and write

$$\xi_0 = (4\pi r_0 \sin\beta)/\lambda, \quad . \quad . \quad . \quad . \quad (2{\cdot}3)$$

we can write the contribution to F from a non-circular orbit as

$$C_2(\xi_0) = \oint \frac{\sin \xi_0 r'}{\xi_0 r'} \frac{df}{dr'} dr', \quad . \quad . \quad . \quad (2{\cdot}4)$$

a function of ξ_0 only, *i. e.* a function of the maximum radius r_0 only, for a given value of $(\sin\beta)/\lambda$. Thus if $C_2(\xi_0)$ is evaluated once for all by integration for some values of ξ_0, and interpolation for other values, and tabulated, then for any particular non-circular orbit of a particular atom it is only necessary to know the maximum radius r_0 and to evaluate ξ_0 and look up $C_2(\xi_0)$ from the table; it is not necessary to carry out the integration $\oint \xi^{-1} \sin\xi \, df$ for each separate orbit at each glancing angle. The saving of numerical work hereby is very considerable.

Certainly on account of the different ratios of minimum radius to maximum radius of different orbits, the values of df/dr' for different orbits differ most for small values of r', for which the value of $\xi^{-1}\sin\xi$ is greatest, but the fraction of a radial period spent in this part of the orbit is always small, and numerical investigation shows that the error involved in assuming the same $(df/dr'\, r')$ curve for all orbits is not serious.

If, corresponding to the contribution $C_2(\xi_0)$ to F from a non-circular orbit, we write the contribution from a circular orbit (for which $\xi = \xi_0$),

$$C_1(\xi_0) = \xi_0^{-1} \sin\xi_0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2{\cdot}5)$$

then (2·2) becomes

$$F = \Sigma_1 C_1(\xi_0) + \Sigma_2 C_2(\xi_0), \quad . \quad . \quad . \quad (2{\cdot}6)$$

suffixes 1 and 2 referring to circular and non-circular orbits respectively.

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§ 3. *Numerical Data on Dimensions of Core Orbits.*

By numerical analysis of the terms of the optical and X-ray spectra, it is possible to obtain a rough idea of the field of an atom, and from this field the dimensions of and progress of time in the core orbit can be calculated. The general lines of this analysis and preliminary results for Na, K, and Ca^+ have been given by the writer in an earlier paper*: the numerical work has since been revised, and similar work carried out for Cl^- (roughly), Cu, Rb, Cs, and Tl. The results must be considered as still subject to revision, but so long as the general ideas on which this work is based are retained, it does not seem probable that any modifications will seriously affect the calculated dimensions of the core orbits, which are the quantities required for the purposes of this paper.

There are two main results of this calculation of core orbits :—

(*a*) The determination of df/dr' as a function of r' for non-circular orbits.

(*b*) The values of the maximum radii of the different core orbits.

The first is only concerned with relative times and dimensions of different orbits, the second with absolute values of the dimensions.

The great similarity of the $(df/dr', r')$ curves for different non-circular core orbits is shown by fig. 1, in which points on the curves for various orbits of various atoms are plotted (the diagram would be too confused if the whole curve for each orbit were drawn). The curve drawn is an average one †, which has been used in the evaluation of the function C_2.

As to the actual dimensions of orbits of the core electrons, one result of the numerical analysis is that the maximum radii of all non-circular core orbits with the same

* D. R. Hartree, Proc. Camb. Phil. Soc. xxi. p. 625 (1923).

† The curve for any actual orbit has a vertical asymptote at the minimum value of r', which is different for different orbits; the average curve has been drawn to stop at $r'=0{\cdot}05$, without a vertical asymptote. The curves for the actual orbits differ little for $r'>0{\cdot}2$, and the maximum fraction of a radial period spent within this radius is about 0·06; this is also the maximum possible error in C_2 due to the assumption that (df/dr') is the same function of r' for all core orbits; actually it seems unlikely that the error will ever be greater than 0·03.

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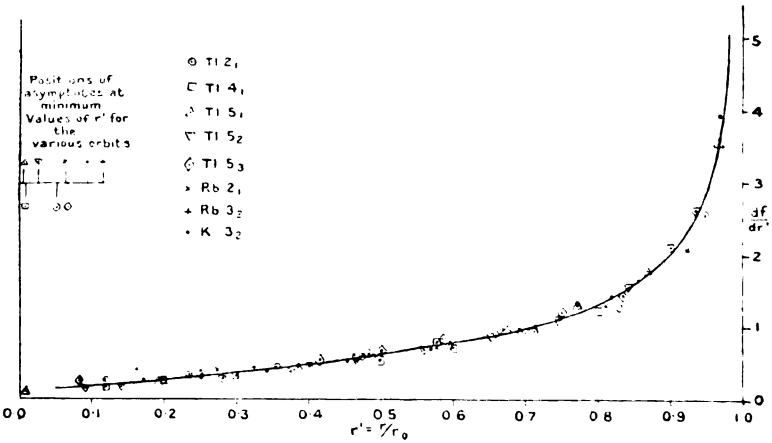
principal quantum number n are very nearly the same *. This again shortens the numerical work of calculating F for any given atom, since—taken in conjunction with the result that the contribution to F from a non-circular orbit is a function of the maximum radius of the orbit only—it means that all non-circular core orbits with the same value of n can be treated as equivalent, so far as their contributions to F are concerned; it is not necessary to consider orbits with different values of k separately. This is not exact, but the error is less than the probable error of determination of the maximum radii of the separate core orbits from the numerical analysis.

Fig. 1.

Showing similar progress of time in all non-circular core orbits.



The vertical lines in Scale A show the positions of the vertical at the minimum radii of the various orbits.

df=fraction of a radial period spent between fractions r' and $r'+dr'$ of the maximum radius r_0.

$\frac{df}{dr'}$ is plotted against r' for various core orbits of various atoms, and a mean curve is drawn.

For different atoms, it seems probable that r_k, the radius of the circular k-quantum core orbit, should vary with

* For example, for Tl the calculated maximum radii of the 4_1, 4_2, and 4_3 core orbits are 0·50, 0·53, and 0·52 times the radius of the 1_1 orbit of hydrogen; the differences between these values are less than the amounts by which they may be in error. It may perhaps be mentioned that the calculations for different values of k are carried out almost entirely independently of one another.

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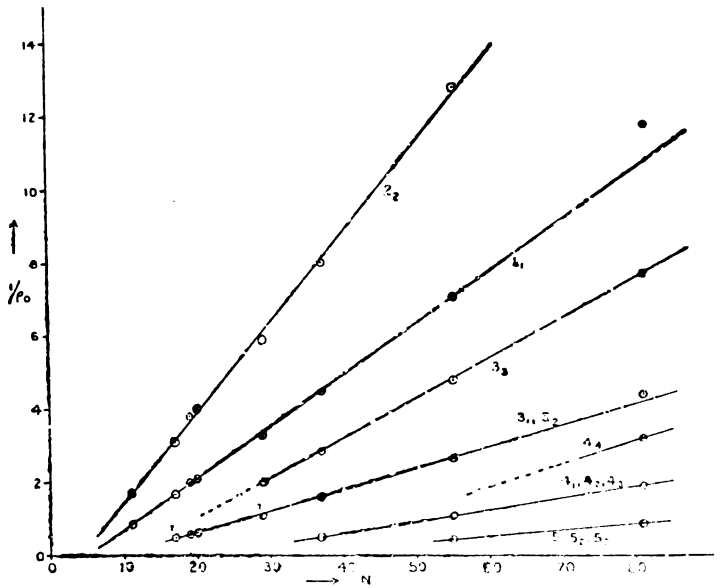
atomic number N approximately according to the relation *

$$r_k\,(\mathrm{N}-\gamma_k) = \text{const.}, \quad . \quad . \quad . \quad . \quad (3{\cdot}1)$$

where γ_k is independent of N, so that $1/r_k$ should be linear in the atomic number N; and it might be expected that a similar relation would hold for the maximum radius of the non-circular orbit with given quantum numbers n_k, except perhaps in that part of the periodic table where the group of principal number n is being built up—more strictly, where the number of electrons in the group of principal quantum number n varies with the atomic number.

Fig. 2.

Showing relation between maximum radii of core orbits and atomic number.



ρ_0 = maximum radius of orbit as multiple of radius of 1_1 orbit of H atom. Calculated values of $1/\rho_0$ plotted against atomic number N.

Writing a for the radius of the 1_1 orbit of the H atom (0·532 Å.U.), and $r = a\rho$, the calculated values of $1/\rho$ for the radii of the circular core orbits and the maximum radii of the non-circular core orbits, of all atoms for which a numerical analysis of the spectra have been made by the writer, are plotted against the atomic number N in fig. 2.

* See D. R. Hartree, Proc. Roy. Soc. cvi. p. 552 (1924).

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The agreement with the theoretical relation is most satisfactory, considering the approximate nature of the analysis and the fact that the calculations for the different atoms are quite independent of one another. This agreement suggests that it is probably fairly safe to use the straight lines given in the diagram in order to interpolate the radii of core orbits of the atoms for which calculations have not yet been made.

§ 4. *Calculation of* F-*Curves.*

The numerical data considered in the previous section will now be given in the form most convenient for the calculation of F-curves.

TABLE I.

Values of $C_1(\xi_0)$ for contributions to F from Circular Orbits.

$\xi_0 = (4\pi r_0 \sin\beta)/\lambda.$ β = glancing angle,

$C_1(\xi_0) = \xi_0^{-1} \sin \xi_0.$ = half angle of scattering.

ξ_0	·0	·1	·2	·3	·4	·5	·6	·7	·8	·9
0	1·00	1·00	0·99	0·98	0·97	0·96	0·94	0·92	0·90	0·87
1	0·84	0·81	0·78	0·74	0·70	0·66	0·62	0·58	0·54	0·50
2	0·45	0·41	0·37	0·32	0·28	0·24	0·20	0·16	0·12	0·08
3	0·05	0·01	−0·02	−0·05	−0·08	−0·10	−0·12	−0·14	−0·16	−0·18
4	−0·19	−0·20	−0·21	−0·21	−0·22	−0·22	−0·22	−0·21	−0·21	−0·20
5	−0·19	−0·18	−0·17	−0·16	−0·14	−0·13	−0·11	−0·10	−0·08	−0·06
6	−0·05	−0·03	−0·01	0·00	0·02	0·03	0·05	0·06	0·07	0·08
7	0·09	0·10	0·11	0·12	0·12	0·12	0·13	0·13	0·13	0·13
8	0·12	0·12	0·11	0·11	0·10	0·09	0·08	0·08	0·07	0·06
9	0·05	0·04	0·02	0·01	0·00	−0·01	−0·02	−0·03	−0·04	−0·05
10	−0·05	−0·06	−0·07	−0·07	−0·08	−0·08	−0·09	−0·09	−0·09	−0·09
11	−0·09	−0·09	−0·09	−0·08	−0·08	−0·08	−0·07	−0·07	−0·06	−0·05
12	−0·05	−0·04	−0·03	−0·02	−0·01	−0·01	0·00	0·01	0·02	0·02
13	0·03	0·04	0·05	0·05	0·06	0·06	0·06	0·07	0·07	0·07
14	0·07	0·07	0·07	0·07	0·07	0·06	0·06	0·06	0·05	0·05
15	0·04	0·04	0·03	0·03	0·02	0·01	0·01	0·00	−0·01	−0·01
16	−0·02	−0·02	−0·03	−0·03	−0·04	−0·04	−0·05	−0·05	−0·05	−0·06
17	−0·06	−0·06	−0·06	−0·06	−0·06	−0·06	−0·05	−0·05	−0·05	−0·05
18	−0·04	−0·04	−0·03	−0·03	−0·02	−0·02	−0·01	−0·01	0·00	0·00
19	0·01	0·01	0·02	0·02	0·03	0·03	0·04	0·04	0·04	0·04
20	0·05	0·05	0·05	0·05	0·05	0·05	0·05	0·05	0·05	0·04

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TABLE II.

Values of $C_2(\xi_0)$ for contributions to F from Non-circular Orbits.

$\xi_0 = (4\pi r_0 \sin\beta)/\lambda.$ β = glancing angle,

$C_2(\xi_0) = \oint \frac{\sin \xi_0 r'}{\xi_0 r'} \frac{df}{dr'} dr'.$ = half angle of scattering.

ξ_0	·0	·1	·2	·3	·4	·5	·6	·7	·8	·9
0	1·00	1·00	0·99	0·99	0·98	0·97	0·96	0·95	0·93	0·92
1	0·90	0·88	0·86	0·83	0·81	0·78	0·75	0·72	0·69	0·66
2	0·63	0·60	0·57	0·54	0·51	0·48	0·44	0·41	0·38	0·35
3	0·32	0·29	0·27	0·24	0·21	0·19	0·17	0·14	0·12	0·10
4	0·08	0·06	0·04	0·03	0·02	0·01	0·00	−0·01	−0·02	−0·03
5	−0·03	−0·03	−0·04	−0·04	−0·04	−0·04	−0·04	−0·04	−0·03	−0·03
6	−0·03	−0·02	−0·02	−0·01	−0·01	0·00	0·00	0·01	0·02	0·02
7	0·03	0·03	0·04	0·04	0·05	0·05	0·06	0·06	0·06	0·06
8	0·07	0·07	0·07	0·07	0·07	0·07	0·07	0·07	0·07	0·06
9	0·06	0·06	0·06	0·05	0·05	0·05	0·04	0·04	0·03	0·03
10	0·03	0·02	0·02	0·02	0·01	0·01	0·00	0·00	0·00	−0·01
11	−0·01	−0·01	−0·01	−0·01	−0·01	−0·02	−0·02	−0·02	−0·02	−0·02
12	−0·01	−0·01	−0·01	−0·01	−0·01	−0·01	−0·01	0·00	0·00	0·00
13	0·00	0·01	0·01	0·01	0·01	0·01	0·01	0·02	0·02	0·02
14	0·02	0·02	0·02	0·03	0·03	0·03	0·03	0·03	0·03	0·03
15	0·03	0·02	0·02	0·02	0·02	0·02	0·02	0·02	0·02	0·01
16	0·01	0·01	0·01	0·01	0·00	0·00	0·00	0·00	0·00	0·00
17	−0·01	−0·01	−0·01	−0·01	−0·01	−0·01	−0·01	−0·01	−0·01	−0·01
18	−0·01	−0·01	−0·01	−0·01	−0·01	−0·01	−0·01	−0·01	0·00	0·00
19	0·00	0·00	0·00	0·00	0·00	0·00	0·01	0·01	0·01	0·01
20	0·01	0·01	0·01	0·02	0·02	0·02	0·02	0·02	0·02	0·02

First, in Tables I. and II. are tabulated the values of $C_1(\xi_0)$ and $C_2(\xi_0)$, the contributions to F from a circular and non-circular orbit respectively ; they are given by

$$C_1(\xi_0) = \xi_0^{-1} \sin \xi_0, \quad . \quad . \quad . \quad . \quad . \quad (2\cdot5)$$

$$C_2(\xi_0) = \oint \frac{\sin \xi_0 r'}{\xi_0 r'} \frac{df}{dr'} dr'. \quad . \quad . \quad . \quad (2\cdot4)$$

In evaluating C_2, the function df/dr' given by the curve in fig. 1 has been used. C_1 and C_2 are tabulated to two decimal

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places, so the numerical error in F is of the order of 1 per cent. of the total number of electrons in the scattering atom; this is less than the possible error due to the approximations made in treating df/dr^j as the same for all non-circular core orbits, and in estimating the actual dimensions of the orbits.

If ρ_0 is the maximum value of ρ for any orbit (i.e. $r_0 = a\rho_0$), then for reflexion of X-rays of wave-length λ at glancing angle β the argument ξ_0 of the function C_1 or C_2 giving the contribution to F from the orbit is, from (2·3),

$$\xi_0 = (4\pi a\rho_0 \sin\beta)/\lambda,$$
$$= (6{\cdot}68\rho_0 \sin\beta)/\lambda, \quad . \quad . \quad . \quad . \quad (4{\cdot}1)$$

if λ is measured in Å.U.

It will be noticed that in so far as ξ_0, and therefore F, is a function of the wave-length λ and the glancing angle β, it depends only on the value of $(\sin\beta)/\lambda$, so that if F is plotted as a function of $\sin\beta$ for any wave-length, the curve for any other wave-length will be found by a simple change of scale of $\sin\beta$. It would, of course, be possible to plot F as a function of $(\sin\beta)/\lambda$, but it will probably be found most convenient in practice to calculate and plot F as a function of $\sin\beta$ for some standard λ (*e.g.* Rh or Mo Kα).

In order to have enough points on the F-curve, it is advisable to calculate F for a set of values of $\sin\beta$ such that successive values of $(\sin\beta)/\lambda$ do not differ by much more than 0·1, if λ is measured in Å.U. For example, for Rh Kα X-rays ($\lambda = 0{\cdot}615$ Å.U.) it is best to calculate F for values of $\sin\beta$ which are multiples of 0·05; if it is only calculated for $\sin\beta = 0{\cdot}1, 0{\cdot}2, 0{\cdot}3 \ldots\ldots$, the points are too far apart to define an F-curve properly.

The values of ρ_0 for the various orbits could be found by reading off values of $1/\rho_0$ from fig. 2, but on account of the rather small scale of the diagram it is probably more satisfactory to use formulæ deduced by fitting linear relations between $1/\rho_0$ and N, using a larger scale diagram. If we write

$$\rho_0 = K/(N-\gamma),$$

then K and γ are functions of the quantum numbers n_k; values of K and γ for the straight lines drawn in fig. 2 are given in Table III. For circular orbits in a central field we must have $K = k^2$. This has been kept in mind in drawing the lines in fig. 2.

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TABLE III.

Data for the Approximate Calculation of Maximum Radii of Core Orbits.

Max. radius $r_0 = a\rho_0$, where a is radius of 1_1 orbit of hydrogen atom.

$\rho_0 = K/(N-\gamma)$, where K and γ are approximately the same for core orbits of the same quantum numbers in different atoms.

Table gives values of K and γ.

Orbit.	K.	γ.
1_1	1·0	1·0
2_1	7·0	5·2
2_2	4·0	4·2
$3_1, 3_2$	17·0	9·5
3_3	9·0	12·0
$4_1, 4_2, 4_3$	32	20·5
4_4	16	30
$5_1, 5_2$	54	32

The only other question we have to consider is the distribution of electrons among the different n_k orbits; and since, so far as their contribution to F is concerned, all the non-circular orbits with the same principal quantum number are equivalent to the order of accuracy required, all we need to know is the distribution of electrons in the circular and non-circular orbits.

Two general arrangements of electrons have been suggested—one by Bohr *, based chiefly on arguments as to symmetry, and concerned with the distribution of electrons among groups characterized by the two quantum numbers n_k; and one recently by Stoner †, from considerations of inner quantum numbers and from experimental evidence, in which the distribution of electrons among groups characterized by the three quantum numbers $n_{k,j}$ is considered. The interpretation of the quantum numbers—especially the inner quantum number j—cannot be taken as yet certain, but assuming that for both distributions the quantum numbers n_k can be correlated with the ordinary principal and azimuthal quantum numbers of an orbit in a central field, the circular orbits are given by $n=k$ and the non-circular by $n \neq k$.

On this assumption the distribution of electrons between the circular and non-circular orbits according to the two schemes is given in Table IV. for the inert gases (and ions of the alkali metals) and for the ions Cu^+, Ag^+, and Au^+, which represent important stages in the building-up of atoms.

* N. Bohr, *Zeit. f. Phys.* ix. p. 1 (1922), or 'The Theory of Spectra and Atomic Constitution,' Third Essay.

† E. C. Stoner, Phil. Mag. xlviii. p. 719 (1924).

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TABLE IV.

Distribution of Electrons in Circular and Non-Circular Orbits in Various Atoms and Ions.

Atom or Ion.	Number of Electrons.	According to Bohr.						According to Stoner.					
		$n=1.$	2	3	4	5	6	1	2	3	4	5	6
		$k=1.$	1 2	1.2 3	1,2,3 4	1,2,3	1,2	1	1 2	1,2 3	1,2,3 4	1,2,3	1,2
He, Li^+...	2	2						2					
Ne, Na^+...	10	2	4 4					2	2 6				
A, K^+ ...	18	2	4 4	8				2	2 6	8			
Cu^+ ...	28	2	4 4	12 6				2	2 6	8 10			
Kr, Rb^+...	36	2	4 4	12 6	8			2	2 6	8 10	8		
Ag^+...	46	2	4 4	12 6	18			2	2 6	8 10	18		
Xe, Cs^+...	54	2	4 4	12 6	18	8		2	2 6	8 10	18	8	
Au^+...	78	2	4 4	12 6	24 8	18		2	2 6	8 10	18 14	18	
Nt, 87^+ ...	86	2	4 4	12 6	24 8	18	8	2	2 6	8 10	18 14	18	8

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TABLE V.

Calculated Values for F for Various Ions as Functions of the Glancing Angle for Mo Kα X-Rays (λ=0·71 Å.U.).

Ion.	sin β for Mo Kα.														
	0·00	0·05	0·10	0·15	0·20	0·25	0·30	0·35	0·40	0·45	0·50	0·55	0·60	0·65	0·70
C^{+2}	2·0	2·0	2·0	2·0	2·0	1·9	1·9	1·9	1·8	1·8	1·7	1·7	1·6	1·6	1·5
O^{-2}	10·0	9·4	8·2	6·4	4·8	3·5	2·4	1·5	0·9	0·6	0·6	1·0	1·4	1·8	2·1
Na^{+}	10·0	9·8	9·4	8·7	8·0	7·0	6·0	5·1	4·1	3·3	2·6	2·1	1·6	1·3	1·0
Si^{+4}	10·0	9·9	9·7	9·5	9·1	8·5	7·9	7·3	6·5	5·9	5·1	4·5	3·9	3·3	2·9
S^{+6}	10·0	9·9	9·8	9·6	9·3	8·9	8·5	8·0	7·5	6·9	6·3	5·7	5·1	4·6	4·1
S^{-2}	18·0	16·7	13·7	10·7	9·1	8·7	8·8	8·6	7·7	6·8	6·2	5·8	5·3	4·7	4·0
Cl^{-}	18·0	17·0	14·5	11·8	9·7	8·8	8·7	8·7	8·4	7·7	6·8	6·2	5·9	5·4	4·9
K^{+}	18·0	17·3	15·6	13·5	11·3	9·6	8·7	8·4	8·4	8·3	8·0	7·5	6·8	6·1	5·3
Ca^{+2}	18·0	17·5	16·0	14·1	12·0	10·4	9·2	8·5	8·4	8·4	8·3	7·9	7·5	6·9	6·0
Cu^{+}	28·0	27·7	27·0	25·8	24·1	22·2	20·2	18·1	16·1	14·0	12·0	10·3	9·0	7·9	6·9
Sr^{+2}	36·0	35·2	33·2	30·6	27·8	25·5	23·8	22·6	21·8	20·6	19·3	17·7	16·0	14·4	13·1
Ba^{+2}	54·0	52·6	49·1	44·8	40·7	37·4	34·8	32·5	29·9	27·4	24·6	23·1	21·9	21·1	20·4
Tl^{+3}	78·0	77·1	75·2	72·0	68·1	63·4	58·8	54·4	50·3	46·8	43·7	40·9	38·8	37·0	34·7

Stoner's distribution of electrons in core orbits has been assumed in calculating the above figures.
F for zero glancing angle is equal to the number of electrons in the ion.

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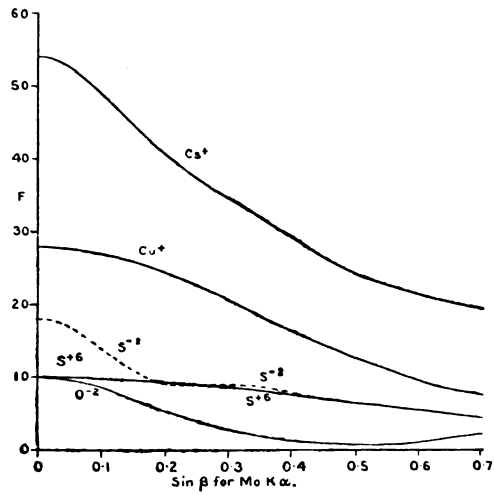
The differences between the values of F calculated from the two distributions are not usually very large; expressed as a fraction of the whole value of F they are most important for the lighter atoms, and particularly for the negative ions with the neon structure (*e.g.* O^{--}). For the numerical examples of F-curves given in this paper, Stoner's distribution will be used unless the contrary is specified.

§ 5. *Some Numerical Results.*

Values of F as a function of the glancing angle β for Mo Kα radiation, calculated from the data of § 4, are given

Fig. 3.



F-curves for various ions. Calculated values of F are plotted against the sine of the glancing angle β for Mo Kα X-rays.

for various ions in Table V.*, and F-curves for some of these ions are shown in fig. 3. The F-curves show two striking features: firstly there is the slow initial decrease of F with increasing glancing angle for the compact ions (such as Cu^{+}, S^{+6}), compared with that for the ions of greater size (*e.g.* Cs^{+}, O^{-2}); and secondly there is the very small difference between the values of F for the same element in different

* The differences between the values for both Na^{+} and Cl^{-} and the values given by the writer in a previous paper (Phil. Mag. *loc. cit.*) are due partly to a revision of orbital dimensions and partly to the adoption of Stoner's distribution of electrons in core orbits.

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states of ionization, except for small glancing angles. These features could both have been predicted from considerations of the general form of the contributions to F from the outer orbits of the atom.

Apart from these it does not seem possible to draw any quantitative generalization from these curves, and for practical application it seems best to calculate the F-curve for each ion as it is required.

§ 6. *Discussion.*

It has been assumed in the above method of calculating F-curves that the electrons in an atom scatter X-rays like free electrons in their instantaneous positions would do on the classical theory.

Two doubts arise in connexion with this assumption: firstly, are we justified in applying classical laws to the scattering of X-rays at all; and secondly, even if the scattering by the loosely-bound electrons can be treated as classical, is classical scattering applicable to electrons bound in orbits of energy of the order of (or greater than) the quantum energy of the incident X-rays?

As to the second of these points, if it is assumed that some electrons (*e.g.* those in K orbits) do not contribute to the radiation scattered (as it seems) classically by the atom as a whole, it is probably best to omit their contributions entirely in evaluating F. For the ordinary X-rays used in crystal analysis, only the K electrons of the heavier elements and perhaps the L electrons of the heaviest would have to be neglected for this reason; as the values for F for these atoms is always considerable, the proportional change in F is not very important.

The question whether even the loosely-bound electrons can be taken as scattering classically is more fundamental and more difficult. All the evidence from the consistent results of X-ray analysis of crystals suggests that each atom scatters a wavelet which interferes classically with those scattered by other atoms; a striking example is the absence of the first-order (111) reflexion from KCl. Further, if we assume classical scattering by an atom as a whole, and assign to each atom a number F representing the ratio of the amplitude of the wave scattered by the atom to that of the wave scattered classically by a free electron, the experimental work of Bragg, James, and Bosanquet * on NaCl shows that F varies with the glancing angle in at any rate the same sort of way

* *Loc. cit.*

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as would be calculated by the methods of § 4 of this paper, assuming classical scattering by the individual electrons in each atom.

Certainly there is a considerable difference between the observed and calculated values of F for both Na^+ and Cl^-, the observed values being smaller than the calculated ones whether Bohr's or Stoner's distribution of electrons is assumed, as is shown in Table VI.; for O^{-2} the observed

TABLE VI.

Comparison of Observed and Calculated Values of F for O^{-2}, Na^+, and Cl^-.

sin β (for Mo Kα)		0·15	0·2	0·25	0·3	
$F(O^{-2})$	obs.	5·6	3·9	2·6	1·5	
	calc. (S)	6·4	4·8	3·5	2·4	
	calc. (B)	5·5	3·9	3·0	2·3	
sin β (for Rh Kα)		0·1	0·2	0·3	0·4	0·5
$F(Na^+)$	obs.	8·3	5·4	3·4	2·0	0·8
	calc. (S)	9·4	7·6	5·6	3·7	2·4
	calc. (B)	9·1	6·9	4·7	3·1	2·2
$F(Cl^-)$	obs.	12·7	7·9	5·8	4·4	3·2
	calc. (S)	13·8	9·1	8·6	7·5	5·9
	calc. (B)	13·7	8·8	8·2	7·0	5·3

(S) = Stoner's distribution of electrons assumed.
(B) = Bohr's " " " "

values* of F are smaller than the values calculated with Stoner's distribution of electrons, in very much the same way as the values for Na^+ and Cl^-; for small glancing angles the observed values agree with those calculated on Bohr's

* In a recent paper (Phil. Mag. xlix. p. 1225 (1925) A. J. Bradley has given some figures for the scattering power of O^{-2}, relative to $K^+ + S^{+6} = 28$; I have taken these figures, interpolated for exact values of sin β for the Mo Kα radiation used, and multiplied by the ratio of the sum of the calculated values of F for K^+ and S^{+6} (Table V.) to 28, to obtain the values of F for O^{-2} given in Table VI. The actual values of F for K^+ and S^{+6} are probably smaller than the calculated values, so that the actual values for O^{-2} are probably smaller than the "observed" values.

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distribution of electrons *, but for larger glancing angles the observed values are smaller, as for the other ions. But the effects of some of the other variables which affect the intensity of reflexion are not yet properly known (the effect of primary extinction † is the most important at small glancing angles, and the effect of the heat-motion the most important at large glancing angles), and possibly have not been properly allowed for in reducing the experimental results to obtain values of F. It is also possible, however, and such evidence as there is at present seems to point to the conclusion, that for some reason at present unexplained the actual values of F are smaller than those calculated on the assumption of classical scattering by the individual electrons; but if such scattering is not assumed, it is difficult to see how a variation of F with glancing angle is to be explained, and it is also not clear why the values of F for small glancing angles should agree at least approximately with those calculated, assuming classical scattering.

For the analysis of crystal structure it is at present impracticable to correct the measured intensities of reflexion for the effects of heat-motion or of primary or secondary extinction; and any difference between actual and calculated values of F will simply give rise to another factor in that part of the variation of intensity of reflexion with glancing angle which it is not practicable to evaluate for each particular case in the determination of crystal structure. For clearness let us consider the intensity of reflexion written in the form of a product of two functions, ϕ_1 and ϕ_2, of the variables on which it depends, the function ϕ_1 being one which it is practicable to evaluate for given values of its arguments in practical crystal analysis, and the function ϕ_2 being one which depends on the variables in such a way that it is not practicable to evaluate it. The effects of heat-motion and extinction have at present to be taken into account by the second function ϕ_2, and so far the same is true of the variation of F with glancing angle. It is hoped that the use of calculated values of F will make it possible to take into account at least part of the variation of F with glancing angle in ϕ_1, leaving only the difference between actual and calculated values of F

* This agreement must not be taken as significant, as the "observed" values of F for O^{-2} are based on values of F for K^+ and S^{+6} calculated using Stoner's distribution of electrons, and are probably too large (see previous footnote).

† See C. G. Darwin, Phil. Mag. xliii. p. 800 (1922), or Bragg, James, and Bosanquet (*loc. cit.* 3rd paper, p. 446) for explanation of primary and secondary extinction.

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to be taken care of by ϕ_2, and so reducing the range of variation of this function.

§ 7. *Summary.*

In the analysis of the more complicated crystal structures by means of X-rays, it is important to know the F-curves of the atoms concerned, *i. e.* the relations between the scattering power F of an atom, defined as the ratio of the amplitude of the wavelet scattered by the atom to that scattered by an electron, and the glancing angle. Assuming that the individual electrons of the atoms in a crystal scatter classically, the F-curve for any given atom can be calculated from the dimensions of and progress of time in the core orbits; for some atoms the atomic field can be found approximately by numerical analysis of the optical and X-ray spectra, and the core orbits can then be calculated; it is possible to generalize the results and put them in such a form that an approximate F-curve for any atom (or rather ion) can be calculated very simply. Numerical results for some ions are given.

XXX. *The Interpretation of Intensity Measurements in X-Ray Analysis of Crystal Structure.* [A Note on the paper "The Atomic Structure Factor in the Intensity of Reflexion of X-Rays by Crystals," by D. R. Hartree.]

By W. Lawrence Bragg, *M.A., Langworthy Professor of Physics, The University of Manchester* *.

1. In all methods of crystal analysis by means of X-rays, the final test of the structure which is assigned to the crystal as a result of the X-ray measurements consists in a comparison of the observed intensities of X-ray reflexion by different planes of the crystal structure with intensities which have been calculated for the proposed atomic arrangement. The structure which leads to the best agreement between calculated and observed values is chosen as the closest approximation to the truth. Anyone who is familiar with X-ray analysis will realize the unsatisfactory nature of the assumptions usually made in calculating the intensity of reflexion to be expected from a given atomic arrangement, and the uncertainty of the results due to an ignorance of the laws governing the intensity. Experimental observations can be made with a high order of accuracy, but their interpretation is extremely difficult. One

* Communicated by the Author.

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factor which is highly important takes account of the amount of X-radiation scattered by the atoms through different angles. The assumption is generally made that the relative scattering powers of the atoms are simply proportional to their atomic numbers, but this approximation to the truth is only made in the lack of a more complete knowledge. The paper on the Atomic Structure Factor by Mr. Hartree is extremely interesting, because it gives estimates of the relative scattering power of the atoms based on calculation of orbit-dimensions. Although these estimates may need modification, and other factors which will be referred to below must be taken into consideration in using Mr. Hartree's results, they represent a great advance on the simple assumption of proportionality between scattering power and atomic number. They are extremely interesting in showing, for instance, how fast the effect of negative ions of low atomic weight falls off with increase in glancing angle, when they are compared with atoms of higher atomic weight.

2. The factors which govern the intensity of X-ray reflexion may for convenience be divided into two types. In the first of these must be classed all those factors which cause a general falling away of intensity as the angle of incidence increases. The exact forms which these factors assume depend on the method of analysis which is employed (spectrometer, Debye powder-photograph, rotating crystal method), as these different methods present different geometrical problems. They also depend on the shape of the crystal sample. For the spectrometer method this may be an extended crystal face, or a very small crystal which is bathed in the X-rays. In the powder method a fine column or an extended surface of powder may be employed. A factor must be introduced to represent the allowance for polarization of the scattered radiation. These factors are functions of the glancing angle θ.

In addition to this the intensity is governed by the structure factor S. This is generally defined as the ratio of the wave amplitude due to a complex plane of atoms when the phase difference introduced by atomic position has been taken into account, to the ideal amplitude which would exist were all the atoms centred exactly on the successive planes. It may perhaps be more conveniently defined as the ratio of the actual amplitude to that which would exist if all the electrons of all the atoms were arranged exactly on successive planes, since we are now allowing for electronic as well as for atomic configuration.

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Any expression for the relationship between incident and diffracted radiation depends also on the wave-length of the X-rays employed, on the number of molecules per cubic centimetre, and the number of electrons in the molecule (if this be not already included in the structure factor S). In certain cases it depends on the absorption coefficient of the crystal, and this in its turn is a most complex function, being the sum of the true absorption coefficient μ and an extinction coefficient ϵ which varies with the state of perfection of the crystal structure and with the intensity of reflexion itself.

The Debye effect, or weakening of the spectra due to the heat-motion of the atoms, may perhaps be most conveniently considered as being included in the structure factor S, since its effect on the amplitude may be calculated by the laws of interference which govern the structure factor.

3. The two points about which most uncertainty exists are: (*a*) the correct method of calculating the structure factor S for any given atomic arrangement, (*b*) the relation of the intensity to the structure factor S. In certain cases it is possible to determine atomic positions accurately without making any precise assumptions about scattering power, and with the most approximate experimental determinations of intensity. This is the case for simple structures containing two or three parameters, which can often be evaluated one at a time by considering certain groups of planes, and it is also the case for structures of the elements where the atoms are all alike so that at any given angle they scatter equally. In more complex crystals it is absolutely necessary to make some assumptions in order to fix the atomic positions.

The following point must be emphasized in this connexion. Even though the dependence of intensity on structure factor is so very obscure, an accurate method of calculating the structure factor furnishes by itself a sufficient guide to the analysis of a structure. If the observed intensities show a parallelism to the calculated structure factors when both are arranged in order of increasing glancing angle, the assigned structure must be right. In comparing each plane with the next at a higher angle, a rise in structure factor should correspond to increased intensity, and a fall in structure factor to a decreased intensity. The absence of certain reflexions, which must be accounted for by a very small factor, is in particular a most important indication of

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atomic position. The structure factor depends both on the positions of the atoms and on their scattering powers. Since it is so necessary to know this factor, Mr. Hartree's figures should prove most useful.

In the earlier work on X-ray analysis it was assumed that the intensity of reflexion varied as the square of the structure factor, other factors being equal. This assumption is still made in the analysis of the powder-photographs and of the Laue photographs, and it is probably justifiable in these cases. However, it has long been known as an empirical law that strong reflexions from faces of highly perfect crystals measured by the X-ray spectrometer were more nearly proportional to the structure factor itself*. The law seems to change from one expressed by "$I \propto S$" to one expressed by "$I \propto S^2$," as one passes from the strong spectra of low order to the weak spectra of high order. Discussions of the intensity of reflexion by Darwin† and Ewald‡ suggest reasons for this. Both these authors agree in attributing a departure from the law "$I \propto S^2$" to the fact that regions of the crystal are very highly perfect, so that there are sufficient planes in perfectly regular array to give complete reflexion of the X-rays over a short range of glancing angles. Darwin regards the existence of these small blocks of perfect crystal as giving rise to a high extinction coefficient, the underlying positions of the crystal not having an opportunity of playing their part in reflexion because the absorption of X-rays at the reflecting angle is abnormally large and the upper layers shield those beneath. Some experimental work on rock-salt§ made an estimate of the extinction coefficient ϵ possible, and it was found that

$$I \propto \frac{S^2}{\mu + \epsilon}$$

for this crystal, where the extinction factor ϵ is proportional to the intensity of reflexion I. In the case of rock-salt, which is a highly distorted crystal, ϵ was only about one-half the absorption coefficient μ for the strongest reflexion. In a more perfect crystal ϵ might be much larger than μ. In

* W. H. Bragg, Phil. Trans. Roy. Soc. See also 'X-Rays and Crystal Structure.'

† C. G. Darwin, Phil. Mag. xliii. (May 1922).

‡ P. P. Ewald, *Phys. Zeit.* xxvi. pp. 29–32 (1925).

§ Bragg, James, and Bosanquet, Phil. Mag. xlii. (July 1921).

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this case the law

$$\text{“}I \propto \frac{S^2}{\mu+\epsilon}\text{” may be written “}I \propto \frac{S^2}{\mu+\alpha I}\text{”}$$

where α is a constant. When I is large this becomes a law "$I^2 \propto S^2$" or "$I \propto S$." When I is small it assumes the normal form "$I \propto S^2$."

Ewald shows that, when perfect reflexion of X-rays takes place over a short range, this range is proportional to the structure factor S, so that a highly perfect crystal should give rise to a law

$$I \propto S.$$

The number of perfectly-arranged planes which are necessary to give complete reflexion increases as I diminishes, so that a crystal which obeys Ewald's law for low orders might obey the law "$I \propto S^2$" for the weaker reflexions of high order. This is again in agreement with experience.

These examples show how much caution must be exercised in comparing calculated and observed intensities of reflexion. One is on far surer ground in correlating structure factor and intensity by tabulating both in order of increasing glancing angle and seeing whether they rise and fall together. The necessary data for such a comparison are provided by any means of observing the intensity of reflexion by all planes of the crystal under equal conditions. With the spectrometer this is done, for instance, by comparing them all with some common standard.

5. In testing the figures for the scattering coefficient given in Hartree's paper, there are indications that the actual coefficients fall away rather more rapidly with increasing glancing angle than those which he gives. This may be partly or wholly due to the heat-motions of the atoms, for which no allowance has been made. Figures for sodium, chlorine, and oxygen given in the paper illustrate this point. Nevertheless, the author is convinced that these F-curves are a closer approximation to the truth than the assumption of a scattering power proportional to atomic number, and that with their help more reliable estimates of atomic configuration can be made.

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XXXI. *X-Ray Analysis of Copper-Zinc, Silver-Zinc, and Gold-Zinc Alloys.* By ARNE WESTGREN *and* GÖSTA PHRAGMÉN *.

[Plates VI.–XI.]

1. THE CHEMICAL NATURE OF METALLIC PHASES.

INVESTIGATIONS on metallographic equilibrium diagrams are usually not considered to be complete if they do not result in stating which chemical compounds the phases found represent. This endeavour to label metallic phases by chemical formulæ has probably its root in the idea that it would be possible in this way to obtain a general survey of intermetallic reactions in the same way as order has been brought into other domains of chemistry by the use of chemical notation. As is well known, this attempt has led to little success, nothing except some rather vague rules concerning the intermetallic reactivity having been derived in this way †.

There are many causes for this failure. One of the most important is evidently that methods hitherto used to determine the chemical nature of metallic phases are inadequate, which is most clearly illustrated by the fact that different investigators examining the same system usually differ widely as to the statement of formulæ for the chemical compounds found. To quote an example, some authors have supposed γ-brass to be $CuZn_2$, while others believe that it is a solid solution of zinc in Cu_2Zn_3 ‡. To the γ-phases of the Ag–Zn and Au–Zn systems have been ascribed the formulæ Ag_2Zn_3 and Au_3Zn_5. As will be seen in the following, all these formulæ are incorrect, as none of them is compatible with the fact that the elementary parallelepiped of the phases mentioned contains 52 atoms.

The difficulty in arriving at correct definitions of intermetallic compounds is evidently due to the fact that metal atoms may easily substitute each other in many lattices—*i. e.*, the solubility of the components in many metallic compounds is comparatively high. The domains of homogeneous phases are thus usually extended to relatively wide ranges of

* Communicated by the Authors.

† G. Tammann, *Lehrbuch der Metallographie*, 3. Aufl. Leipzig, 1923, p. 255.

‡ Unlike most investigators of the Cu–Zn system, S. Shepherd has restrained himself from proposing any formulæ for the Cu–Zn phases. He has taken the scientifically more valid standpoint of regarding all the Cu–Zn phases as solid solutions. *Journ. Phys. Chem.* viii. p. 421 (1904).

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composition. In the case of an intermetallic compound dissolving very little or practically nothing of its components, its chemical formula is of course found as soon as its composition is established, but cases of this kind are so rare that they may be regarded almost as exceptional*.

As it might thus rightly be presumed that a great number, if not the majority, of the formulæ hitherto assigned to intermetallic compounds are wrong, it is no wonder that the attempt to find any laws governing intermetallic reactivity on the basis of these chemical symbols has met with little success.

In the following the authors will try to elucidate the question to what extent X-ray analysis may contribute to a deeper insight into the chemical nature of metallic phases. But before that topic is treated, it is necessary to discuss the fundamental question of the differences between solutions and chemical compounds in solid systems.

Different opinions have of late been expressed on this matter. It has been suggested that the term chemical compound loses its physical meaning in ranges of low temperatures, where no diffusion in solid systems is possible, and where thus the only movement of the atoms consists in vibrations about the points of the lattice†. This conception is evidently absurd as, according to this view, substances such as for instance aluminium oxide and sodium chloride would cease to be chemical compounds when cooled down to a sufficiently low temperature. It is highly improbable that at any temperature diffusion would take place within a NaCl-crystal in such a manner that a Na-atom would always move together with a Cl-atom, and yet solid sodium chloride is certainly a chemical compound. A definition of what is essential in solid chemical compounds is evidently not to be based on any assumptions concerning the mobility of their atoms.

W. Rosenhain ‡ has recently put forth the hypothesis of the atoms being more intimately combined in intermetallic compounds than in solid solutions, which would bring about that the interatomic distances in the first-mentioned substances would differ markedly from the normal ones.

* During the examination of ten binary systems by means of X-rays the authors have met with few phases of this kind. The translation group has been determined for three of them, viz. $FeSi_2$, $CuAl_2$, and Fe_3C, the first two of these being tetragonal and the last one orthorhombic.

† G. Tammann, *loc. cit.* p. 832 (1923).

‡ 'Nature,' cxii. p. 832 (1923).

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Confronted with reliable experimental facts, this view has, however, already turned out to be untenable. The distances between the atomic centres in intermetallic compounds do not seem to differ perceptibly from those in other crystals. Rosenhain's supposition has evidently its origin in the very common idea that the forces holding together atoms in an intermetallic compound are of another kind, or at least stronger than those acting between atoms in a pure metal or in a solid solution. The validity of this view has, however, never been proved. The bonds probably being non-polar in all cases, there seems to be no reason not to believe that the interatomic forces should be essentially the same in a solid solution as in a compound. They are certainly as "chemical" in the one case as in the other.

According to the authors' opinion, the fundamental difference between solid chemical compounds and solid solutions lies in their structure. *In an ideal chemical compound structurally equivalent atoms are chemically identical. In an ideal solid solution all atoms are structurally equivalent.* In the latter case some of the atoms of the solvent are replaced by atoms of another kind, which take the place of the former, and which are distributed quite irregularly in the parent lattice *.

Of these two extreme types of structures the first one seems to occur comparatively seldom in metallic phases, while the second one is met with frequently. A multitude of metallic phases seem, however, to represent an intermediate stage between these two extreme cases, forming what might be characterized as solid solutions in chemical compounds.

Comprehensive investigations on the corrodibility of binary solid solutions have led Tammann † to conclude that in the case of simple proportions between the atomic concentrations of the solute and the solvent the atoms of the former have a tendency to arrange themselves in a regular manner in the parent lattice of the solvent. This adjustment in the structure of solid solutions may, however, be expected to take place only if the alloys are annealed for a considerable time at a temperature just below the melting-point, where the mobility of the atoms is great enough to allow of their changing place.

* In exceptional cases this substitution may be of a *complex* nature (comp. Journ. Inst. Metals, xxxi. p. 204, 1924, and Journ. Iron & Steel Inst. cix. p. 171, 1924).

† G. Tammann, 'Mischkristallreihen und ihre Atomverteilung,' Leipzig, 1919

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The X-ray testing of this hypothesis has led to contradictory results. Several investigators have failed to confirm it *. Bain † has, however, reported the discovery of some supernumerary interferences in the photograms of annealed gold-copper alloys containing 25 atomic per cent. gold or copper, and he thinks these might be explained according to the view of Tammann. Quite recently one of the present authors has also found that in a solid solution of 25 atomic per cent. of silicon in iron the silicon atoms are orientated in a face-centred cubic lattice of a parameter twice that of the body-centred α-iron lattice ‡. At this composition the substituting silicon atoms are thus arranged in a regular manner, and the solid solution is transformed into the chemical compound Fe_3Si.

So far, it has not yet been made out how complete this rearrangement of the dissolved atoms in solid solutions may be, and it is still unknown whether its occurrence is confined only to some very narrow ranges of composition. Of course, it seems most probable, however, that, sometimes at least, the readjustment of the atoms may be only partial, and it takes place even if the composition differs a little from the values where it sets in most easily. This grouping of the atoms would thus also give rise to systems of a kind which, like so many other metallic phases, might be considered to form an intermediate stage between the two ideal structures defined above. A complete readjustment of the atoms causes the formation of an ideal chemical compound.

2. Analogies between Different Metallic Systems.

While examining alloys by means of X-rays §, the authors accidentally came across a very strange resemblance between a Cu–Al phase containing 31 atomic per cent. of aluminium and a Cu–Zn alloy holding about the same atomic percentage of copper ‖. The X-ray photograms, which were very

* P. Scherrer, *Compt. rend. Soc. suisse de Physique*, Schaffhausen, Aug. 27th, 1921. F. Kirchner, *Ann. d. Physik*, [4] lxii. p. 59 (1922). F. Wever, according to G. Tammann, *Ann. d. Physik*, [4] lxxv. p. 214 (1924). A. E. van Arkel, *Physica*, iv. p. 33 (1924).

† Chem. & Met. Eng. xxviii. p. 68 (1923).

‡ G. Phragmén, 'Stahl u. Eisen,' xlv. p. 299 (1925).

§ E. R. Jette, G. Phragmén, and A. F. Westgren, Journ. Inst. Metals, xxxi. p. 193 (1924).

‖ Comp. 'Nature,' cxiii. p. 123 (1924), where X-ray photograms of these alloys are reproduced.

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similar, proved that in both cases the substances were cubic and contained 52 atoms per elementary cube. One of the compounds thus corresponded to Cu_9Al_4 and the other to Zn_9Cu_4.

Such analogies in structure between metallic phases of different composition are evidently common. Already the shape of the equilibrium diagrams gives in some cases evidence of a close relationship between different systems. H. C. H. Carpenter * has thus pointed out how similar the diagrams of the Cu–Zn, Ag–Zn, and Ag–Cd alloys are, and he has suggested an explanation of this fact by assuming an analogous formation of the different phases of these systems.

Problems of this kind might, of course, advantageously be penetrated by means of modern X-ray methods, and the authors have, therefore, in this way investigated the systems Cu–Zn, Ag–Zn, and Au–Zn, which could be supposed to show far-reaching analogies in structure. The melting-point curves and the state of these alloys at ordinary temperature as derived from microscopical examination and from X-ray analysis are schematically demonstrated in fig. 1.

The Cu–Zn diagram in that figure is in entire agreement with that given by S. Shepherd †. The investigation of Ag–Zn has confirmed the results of Carpenter ‡ with the exception that the decomposition of the β-phase into α and γ at about 260° C., stated by him, has not been verified. The Cu–Zn and Ag–Zn systems have been found to be completely analogous; each phase found in one of them has been met with also in the other. All these phases with their different characteristic grouping of atoms recur also in the Au–Zn alloys, but in addition to these there have been found two more phases in the latter system. This is therefore a little more complicated than the other ones, which is in agreement with the Au–Zn diagram recently suggested by P. Saldau §. His diagram has not, however, as will be seen in the following, been verified in all respects.

The Cu–Zn and Ag–Zn alloys have already previously been the subject of some X-ray investigations. E. C. Bain ‖ has determined the lattice dimensions of their α-phases, and

* *Intern. Zeitschr. f. Metallographie*, iii. p. 170 (1913).
† *Loc. cit.*
‡ *Intern. Zeitschr. f. Metallographie*, iii. p. 175 (1913).
§ Journ. Inst. Metals, xxx. p. 351 (1923).
‖ Chem. & Met. Eng. xxviii. pp. 21, 65 (1923).

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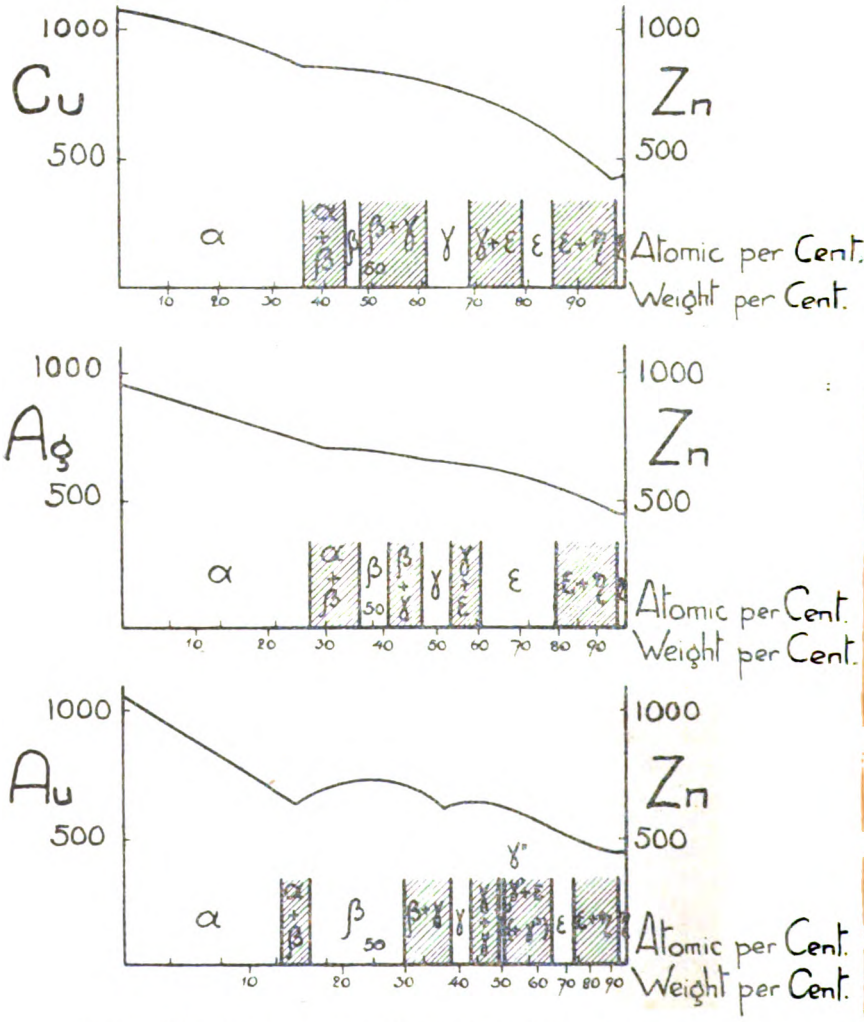
M. R. Andrews *, as well as E. A. Owen and G. D. Preston †, have analysed the Cu–Zn systems throughout its whole

Fig. 1.



Survey of the phases in the Cu–Zn, Ag–Zn, and Au–Zn systems.

* Phys. Rev. xxi. p. 245 (1921).

† Proc. Phys. Soc. Lond. xxxvi. p. 49 (1923). When the work of Owen and Preston was published, the authors had nearly finished their X-ray analysis of the Cu–Zn alloys.

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range. The latter investigations are, however, incomplete as to the γ-brass, as Andrews has totally overlooked this phase, while Owen and Preston have not succeeded in determining its crystal form.

3. Preparation of the Alloys.

The metals used in the investigation were silver and gold containing more than 99·98 per cent. of the pure metal, electrolytic copper, and zinc from Kahlbaum. The meltings were made in porcelain crucibles in a carbon resistance furnace.

Because of their relative expensiveness, the gold alloy specimens could not be made larger than a few grammes. It was, however, found to be quite easy to get even those small meltings sound without using any protecting slag. The zinc mixed with gold was molten very cautiously, after which it dissolved the gold rapidly. At a certain state of dissolution a reaction suddenly occured, through which an amount of heat was liberated, just sufficient to raise the temperature to a point where all the gold was solved. This practice made the loss of zinc through evaporation very small.

When a melting was finished, the crucible with its content was left to cool in the air. It is thus possible that the decrease in temperature in some cases was too rapid to give a state of the alloy corresponding to true equilibrium at ordinary temperature. As the chief purpose of the investigation was not, however, to control the boundary lines of the equilibrium diagrams but to make an examination of the crystal structure of the different phases of the systems, it was nevertheless considered that the alloys in most cases could be used without any further heat treatment.

The composition of the alloys was controlled by chemical determination of the copper, silver, or gold content. It differed only a few tenths of one per cent. from the percentages aimed at in the weighing together of the metals before melting.

4. Experimental Arrangements.

The X-ray apparatus and most of the instruments used have been described in previous papers*. Some new cameras have, however, also been employed which were constructed on the basis of the focussing principle, introduced by H. Bohlin†. His camera type has the

* Journ. Iron & Steel Inst. cvi. p. 241 (1922); cix. p. 159 (1924). Journ. Inst. Metals, xxxi. p. 193 (1924).

† *Ann. d. Physik*, [4] lxi. p. 421 (1920).

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advantage, over the ordinary arrangement for taking powder photograms, that it makes use of the radiation from a larger part of the focus on the target. A considerable increase in dispersion may thus be attained without lengthening the time of the exposure. Some Au–Zn photograms taken in one of these new cameras covering the diffraction range 33–62° are reproduced in fig. 5 (Pl. IX.), and may there be compared with the corresponding photograms obtained in the ordinary camera. The dispersion in the former is about seven times as great as in the latter. Besides this precision camera, another new one of a similar kind has been used photographing the interferences in the range 59–113°. These Bohlin cameras have been calibrated empirically, whereby the fundamental spacing of rock-salt, $d = 5{\cdot}628$ Å., has been used as a basis *.

The mean error of the $\sin^2\frac{\theta}{2}$ values (θ being the diffraction angle), derived from the precision photograms, might be estimated at $\pm$ 0·001 in the ranges 0·070–0·259 and 0·636–0·987, while it might be considered to be $\pm$ 0·002 in the range 0·259–0·636. Being somewhat more uncertain, the $\sin^2\frac{\theta}{2}$ values obtained from the ordinary powder photograms will be marked off by smaller types in the following.

All photograms except the Laue patterns have been taken with iron radiation ($\lambda K_{\alpha 1} = 1{\cdot}932$ Å.; $\lambda K_{\alpha 2} = 1{\cdot}934$ Å.; $\lambda K_{\beta} = 1{\cdot}753$ Å.).

5. Results of the X-Ray Analysis.

The analogy between the three systems displays itself already at a glance at the series of photograms given in figs. 2–4 (Pls. VI.–VIII.). Every kind of diffraction pattern occurring in the Cu–Zn series is met with also in the other ones. Phases denoted in the same way must thus have an analogous structure.

A. *The α-Phases.*

The diffraction patterns of the α-alloys are all of the copper, silver, or gold type, and thus confirm that these phases represent solid solutions of zinc in these metals.

* M. Siegbahn, 'Spektroskopie der Röntgenstrahlen,' Berlin, 1924, p. 20.

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Precision photograms of pure copper and of α-brass containing 32·2 per cent. zinc have been taken beside each other on one and the same plate * (Pl. X. fig. 6, I.). The displacement of the interferences caused by the larger volume of the substituting zinc atoms stands out very distinctly on this plate. The X-ray data obtained from this plate, together with those derived from precision photograms of pure gold and of pure silver, are given in Table I. h_1, h_2, and h_3 denote the Miller indices, d_{100} the edge of the elementary cube, and I the relative intensity of the interferences. The latter is indicated with v.w. = very weak ; w. = weak ; m. = of medium strength ; st. = strong.

TABLE I.

Precision Photogram of Copper, α-Brass (32·2 per cent. Zn), Silver and Gold.

Substance.	I.	$\sin^2\frac{\theta}{2}$.	Radiation.	$h_1h_2h_3$.	$\frac{\sin\frac{\theta}{2}}{\sqrt{h_1^2+h_2^2+h_3^2}}$.	d_{100} in Å.
Copper.	m.	0·6485	K_β	311	0·05895	3·610
	v.w.	0·7075	K_β	222	0·05896	
	st.	0·789	K_α	311	0·07173	
	m.	0·861	K_α	222	0·07175	
α-Brass containing 32·2 % Zn.	st.	0·7575	K_α	311	0·06868	3·688
	m.	0·826	K_α	222	0·06883	
Silver.	st.	0·6745	K_α	222	0·05621	4·080
	m.	0·8765	K_β	331	0·04613	
	m.	0·8985	K_α	400	0·05615	
	m.	0·923	K_β	420	0·04615	
Gold.	st.	0·678	K_α	222	0·05633	4·073
	m.	0·8805	K_β	331	0·04634	
	m.	0·902	K_α	400	0·05638	
	m.	0·9255	K_β	420	0·04628	

The average weight of the atoms constituting the α-brass investigated is $64·14 . 1·650 . 10^{-24}$ g. ($1·650 . 10^{-24}$ g. being the weight of an atom with the atomic weight 1); the density of the alloy determined by weighing in the air and in water has been found to be 8·45, and its lattice parameter is 3·688 Å. (Å. = 10^{-8} cm.). If the number of atoms per elementary cube is calculated on the basis of these data, the number 4·009 is obtained, *i. e.* four within the limits of error. The statement of previous investigators is thus

* Comp. Journ. Inst. Metals, xxxi. p. 202 (1924).

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confirmed that α-brass is formed by a simple substitution of copper by zinc atoms.

The dissolving of 32 per cent. zinc into copper causes an increase in the lattice parameter from 3·610 Å. to 3·688 Å., *i.e.* about 2 per cent. The powder photograms of the corresponding Ag–Zn and Au–Zn phases indicate that the lattices of these alloys are somewhat smaller than the lattices of silver and gold. The zinc atoms are evidently considerably "larger" than the copper atoms, but slightly "smaller" than the gold and silver atoms.

It was considered useless to take precision photograms of the α-Ag–Zn and α-Au–Zn alloys, as their interferences were found to be very cloudy. The real cause of this diffuseness of the lines still remains to be unravelled. Attention might also be drawn to the fact that not even the pure metals—copper, silver, or gold—have given precision photograms of the same distinctness as other substances, such as, for instance, iron or aluminium *. The most deviated K_α-interferences of the latter metals are easily resolved into distinct doublets, but in the precision photograms of Cu, Ag, and Au the $K_{\alpha 1}$ and $K_{\alpha 2}$ lines flow together.

Saldau has found a maximum in the electrical conductivity of the Au–Zn alloys at a composition of 25 atomic per cent. Zn, and from the fact that this maximum shifts at 250° C., he concludes that a transformation takes place at this temperature giving rise to a phase corresponding to the compound Au_3Zn. In order to produce this phase, an alloy having the composition of Au_3Zn was annealed during 10 hours at 250° C.

The powder photogram of the annealed specimen turned out to be exactly identical with that of the unannealed α-phase, and thus did not indicate the existence of any compound Au_3Zn †.

According to previous determinations, the lattice of gold should be somewhat larger than that of silver. Already the ordinary powder photograms indicate, however, and comparative precision photograms have proved conclusively, that the contrary is right. Wh. P. Davey ‡ has recently stated that the lattice parameters of silver and gold are $4·058 \pm 0·004$ and $4·076 \pm 0·004$ Å. respectively. The values found by the authors are, however, for silver 4·080 Å., and

* See Jette, Phragmén, and Westgren, *loc. cit.* p. 200, pl. xviii. V.

† *Note to the proof.*—The authors have later found that an Au-Zn alloy containing about 25 atomic per cent. zinc undergoes a phase change when annealed in a *cold-worked* state.

‡ Phys. Rev. [2] xxiii. p. 292 (1924).

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for gold 4·073 Å. Their mean error might be estimated at $0 \pm \cdot 003$ Å. It seems probable that the silver investigated by Davey has not been quite free from copper.

B. *The β-Phases.*

Andrews, as well as Owen and Preston, have stated that β-brass has a body-centred cubic structure. The powder photogram of this phase obtained by the authors is in fair agreement with that statement. A thin plate was, however, also cut out of a coarse-grained β-brass sample and examined according to the Laue method. When the incident rays were parallel to [100], a Laue pattern (Pl. XI. fig. 7, I.) was produced showing tetragonal symmetry, and when the primary X-ray beam was parallel to [111] a photogram of trigonal symmetry was obtained. As the Cu- and Zn-atoms differ very little in diffractive power, it cannot be settled from the X-ray data if β-brass is to be regarded as an ideal solid solution or not. The powder photograms of β-Ag–Zn and β-Au–Zn prove, however, that the elementary cube in this case is primitive. The relative intensity of the interferences agrees with that calculated on the assumption that the lattice is built up of two simple cubic lattices centring each other (CsCl-structure). It is thus constituted of two groups of atoms, structurally inequivalent, and the β-phases might accordingly be considered to form solid solutions having the compounds CuZn, AgZn, and AuZn for bases.

As to β-brass, this conclusion may, of course, be drawn only if it is presumed that its structure is analogous to that of β-Ag–Zn and β-Au–Zn, but there is no reason to believe anything else. There is thus very little reason for the opinion recently expressed by Rosenhain * that β-brass might be regarded as a solid solution of zinc in a body-centred cubic modification of copper. It is very improbable that β-brass is an ideal solid solution.

Though it might thus be taken almost for granted that β-brass has the compound CuZn as a basis, an alloy of this composition is not homogeneous at ordinary temperature, but consists of a mixture of γ-brass and a phase, corresponding to CuZn, where about 5 per cent. of the zinc atoms are substituted by copper atoms. To form a β-brass that is homogeneous and stable at ordinary temperatures it is thus necessary that a few per cent. of copper are dissolved into CuZn.

* Journ. Inst. Metals, xxx. p. 23 (1923).

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TABLE II.—Powder Photograms of the β-Phases.

Alloy.	I.	$\sin^2\frac{\theta}{2}$.	Radiation.	$h_1h_2h_3$.	$\frac{\sin^2\frac{\theta}{2}}{h_1^2+h_2^2+h_3^2}$.	d_{100} in Å.	Density.	Average Atomic Weight.	Number of Atoms per Elementary Cube.
Cu–Zn 46·9 per cent. Zn.	m.	0·174	K_β	110	0·087	2·945	8·32	64·40	2·000
	st.	0·214	K_α	110	0·107				
	w.	0·355	K_β	200	0·0888				
	st.	0·4305	K_α	200	0·1076				
	m.	0·534	K_β	211	0·0890				
	st.	0·6435	K_α	211	0·1073				
	w.	0·704	K_β	220	0·088				
	st.	0·858	K_α	220	0·107				
Ag–Zn 38·25 per cent. Zn.	v.w.	0·093	K_α	100	0·093	3·156	9·10	86·39	2·007
	w.	0·154	K_β	110	0·077				
	st.	0·187	K_α	110	0·093				
	v.w.	0·202	K_β	111	0·077				
	w.	0·281	K_α	111	0·0937				
	m.	0·310	K_β	200	0·0775				
	st.	0·375	K_α	200	0·0938				
	m.	0·463	K_β	211	0·0772				
	w.	0·470	K_α	210	0·0740				

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	st.	0·5635	K_α	211	0·0939				
	v.w.	0·622	K_β	220	0·078				
	st.	0·754	K_α	220	0·094				
	w.	0·777	K_β	310	0·078				
	w.	0·848	K_α	$\left\{\begin{matrix}300\\221\end{matrix}\right\}$	0·094				
	v.w.	0·931	K_β	222	0·078				
	st.	0·945	K_α	310	0·094				
Au-Zn 30·2 per cent. Zn.	v.w.	0·077	K_β	100	0·077	3·146	13·12	123·73	2·001
	m.	0·093	K_α	100	0·093				
	m.	0·155	K_β	110	0·078				
	st.	0·189	K_α	110	0·095				
	w.	0·2835	K_α	111	0·0945				
	v.w.	0·313	K_β	200	0·078				
	st.	0·3795	K_α	200	0·0949				
	st.	0·470	K_α	210	0·0940				
	st.	0·568	K_α	211	0·0947				
	w.	0·624	K_β	220	0·078				
	st.	0·758	K_α	220	0·094				
	st.	0·850	K_α	$\left\{\begin{matrix}300\\221\end{matrix}\right\}$	0·094				
	st.	0·945	K_α	310	0·095				

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The Laue investigation of the large β-brass grains has proved that they are real crystal individuals. As already stated by H. Imai *, as well as by Owen and Preston, it is therefore very improbable that the thermal effect observed in β-brass at about 470° C. † should be caused by any polymorphic change. The same seems to be the case as to the analogous phenomenon in β-Ag–Zn observed by Carpenter ‡. In any case, the thermal effect in this phase at 260° C. can hardly be explained in the way suggested by him—*i. e.*, by a splitting-up of β into α and γ at this temperature. An AgZn alloy of a composition corresponding to AgZn (41 per cent. Zn) was annealed for 10 hours at 250° C. The powder photogram of this specimen was, however, quite like the photogram of the same alloy quenched in water from the liquid state, and it is thus proved that no crystallographic change had taken place at annealing.

The compound AuZn has a greater capacity than AgZn and CuZn of keeping either of its components in solution at ordinary temperature; for instance, an alloy containing 30·2 per cent. Zn has a homogeneous β-structure. This alloy may thus be considered to be AuZn (25 per cent. Zn), in which every fifth gold atom is replaced by a zinc atom. In spite of the very considerable divergence from the ideal CsCl-structure, the interferences in the powder photogram of this alloy (Pl. VIII. fig. 4, V.) are quite distinct; even those fainter K_α-lines which are caused by the difference in reflective power between the gold and the zinc atoms are plainly visible.

X-ray data of the β-phases are given in Table II.

C. *The γ-Phases.*

A sliver, cut out of a coarse-grained γ-brass specimen (65 per cent. Zn) was investigated according to the Laue method. One of the photograms obtained showed tetragonal (Pl. XI. fig. 7, II.) and another one trigonal symmetry. They both proved that γ-brass is cubic (T_d, O, or O_h) and has a lattice parameter of about 9 A.

The sliver was also mounted in a camera for taking rotation photograms §, and while rotating round one of its

* Science Reports, Tohoku Imp. Univ. xi. no. 5, p. 313 (1922).

† Carpenter & Edwards, Journ. Inst. Metals, v. p. 127 (1911). O. F. Hudson, Journ. Inst. Metals, xii. p. 89 (1914).

‡ *Loc. cit.* p. 159.

§ Journ. Iron & Steel Inst. cix. p. 161 (1924).

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tetragonal axes, it was illuminated by a narrow beam of iron radiation. The diffraction pattern obtained (Pl. XI. fig. 7, III.) contains 81 interference spots (K_α- and K_β-interferences), all in perfect agreement with the equations:

$$\sin^2\frac{\theta}{2} = 0{\cdot}0119\ (h_1^2 + h_2^2 + h_3^2)\ \ldots\ (K_\alpha),$$

$$\sin^2\frac{\theta}{2} = 0{\cdot}0098\ (h_1^2 + h_2^2 + h_3^2)\ \ldots\ (K_\beta).$$

The relative intensity and the indices of the interferences observed in the rotation photogram are given in Table III.

TABLE III.

Photogram of a γ-Brass Crystal rotating about [001].

I.	$h_1h_2h_3$.	I.	$h_1h_2h_3$.	I.	$h_1h_2h_3$.	I.	$h_1h_2h_3$.	I.	$h_1h_2h_3$.
st.	330	w.	321	st.	222	w.	123	w.	224
w.	420	st.	411	w.	312	st.	303	st.	424
m.	510	w.	501	v.w.	402	st.	323	st.	444
v.w.	440	w.	521	m.	332	v.w.	433	w.	534
st.	600	m.	611	m.	422	v.w.	523	w.	604
st.	550	m.	631	w.	512	st.	613	w.	624
m.	640	st.	721	m.	442	w.	543	st.	554? 714
m.	730	w.	651	v.w.	532	st.	633		
m.	800	st.	811? 741	st.	712	w.	703		
st.	820	w.	831	w.	642	m.	733		
st.	660	st.	841	m.	732	m.	653		
w.	750	st.	941	m.	802	m.	813		
m.	840			st.	822	st.	843		
st.	910			st.	662				
				st.	752				

The γ-phases of the three zinc alloys resemble each other strikingly, and are also very like the phase occurring in the range 16 to 25 per cent. aluminium in the copper-aluminium alloys. All these substances are extremely brittle and have a vitreous and lustrous fracture. This likeness is evidently due to a similar grouping of their atoms. The X-ray data, obtained from the powder photograms of γ-brass, γ-Ag–Zn, and γ-Au–Zn are set out in Tables IV. and V.

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TABLE IV.—Powder Photograms of γ-Brass.

I.	$h_1h_2h_3$.	61·7 per cent. Zn.		64·7 per cent. Zn.		67·7 per cent. Zn.	
		$\sin^2\frac{\theta}{2}$.	$\frac{\sin^2\frac{\theta}{2}}{h_1^2+h_2^2+h_3^2}$.	$\sin^2\frac{\theta}{2}$.	$\frac{\sin^2\frac{\theta}{2}}{h_1^2+h_2^2+h_3^2}$.	$\sin^2\frac{\theta}{2}$.	$\frac{\sin^2\frac{\theta}{2}}{h_1^2+h_2^2+h_3^2}$.
w.	222 K_β	0·114	0·0095	0·117	0·0098	0·116	0·0097
w.	222	0·142	0·0118	0·142	0·0118	0·144	0·0120
w.	321	0·164	0·0117	0·164	0·0117	0·166	0·0119
st.	411, 330 K_β	0·173	0·0096	0·173	0·0096	0·177	0·0098
st.	411, 330	0·211	0·0117	0·212	0·0118	0·214	0·0119
v.w.	420	0·230	0·0115	0·236	0·0118	0·233	0·0117
m.	332	0·264	0·01200	0·263	0·01195	0·261	0·0119
w.	422	0·2865	0·01194	0·285	0·01187	0·284	0·0118
w.	510	0·310	0·01192	0·310	0·01192	0·309	0·0119
w.	442, 600 K_β	0·3545	0·00985	0·353	0·00981	0·352	0·0098
st.	442, 600	0·4315	0·01199	0·4305	0·01196	0·426	0·0118
w.	532, 611	0·453	0·01192	0·453	0·01192	0·452	0·0119

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v.w.	444 K_β	0·473	0·00985	0·473	0·00985	0·471	0·0118
w.	633 721 K_β	0·5315	0·00984	0·5295	0·00980	0·524	0·0097
w.	631	0·548	0·01191	0·547	0·01189	0·550	0·0120
m.	444	0·5735	0·01195	0·570	0·01187	0·572	0·0119
w.	550	0·5965	0·01193	0·5955	0·01191	0·596	0·0119
st.	633 721	0·6455	0·01195	0·6435	0·01192	0·642	0·0119
v.w.	642	0·670	0·01195	0·669	0·0119	0·6625	0·01183
v.w.	822 660 K_β	0·707	0·01198	0·704	0·0119		
w.	651 732	0·739	0·01192	0·741	0·0120	0·734	0·01184
st.	554 ? 741 811 ?	0·788	0·01192	0·789	0·0120	0·781	0·01183
w.	644 ? 820	0·811	0·01193	0·809	0·0119	0·8055	0·01185
v.w.	653	0·834	0·01192	0·834	0·0119	0·8285	0·01184
st.	822 660	0·8595	0·01194	0·859	0·0120	0·851	0·01182
w.	750 831	0·8835	0·01194	0·882	0·0119	0·8765	0·01184
w.	662	0·906	0·01192	0·909	0·0120	0·902	0·01187
v.w.	752	0·9305	0·01193	0·930	0·0119	0·9255	0·01187

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TABLE V.—Powder Photograms of γ-Ag-Zn and γ-Au-Zn.

Ag-Zn. 50·3 per cent. Zn.				Au-Zn. 36·9 per cent. Zn.				Au-Zn. 41·1 per cent. Zn.	
I.	$h_1h_2h_3$.	$\sin^2\frac{\theta}{2}$.	$\frac{\sin^2\frac{\theta}{2}}{h_1^2+h_2^2+h_3^2}$.	I.	$h_1h_2h_3$.	$\sin^2\frac{\theta}{2}$.	$\frac{\sin^2\frac{\theta}{2}}{h_1^2+h_2^2+h_3^2}$.	$\sin^2\frac{\theta}{2}$.	$\frac{\sin^2\frac{\theta}{2}}{h_1^2+h_2^2+h_3^2}$.
v.w.	211 K_β 210?	0·056	0·0092 0·0112	w.	211	0·065	0·0108	0·066	0·0110
v.w.	211	0·067	0·0112	v.w.	220			0·088	0·0110
w.	222	0·131	0·0109	m.	411 330 K_β	0·160	0·0089	0·164	0·0091
m.	411 330 K_β	0·160	0·0089	st.	411 330	0·194	0·0108	0·200	0·0111
st.	411 330	0·195	0·0108	w.	420			0·221	0·0111
w.	332	0·239	0·0109	w.	332	0·236	0·0107	0·241	0·0109
w.	422	0·259	0·01079	m.	422	0·2615	0·01090	0·265	0·01103
v.w.	510	0·2785	0·01071	v.w.	510	0·2835	0·01090	0·285	0·01094
w.	442 600 K_β	0·3175	0·00882	m.	442 600 K_β	0·323	0·00897	0·326	0·00906
w.	440	0·342	0·01069	w.	532 611 K_β	0·3395	0·00894	0·342	0·00901
st.	442 600	0·389	0·01080	v.w.	440			0·354	0·01103
w.	532 611	0·4095	0·01078	v.w.	530? 433			0·374	0·01100
				st.	442 600	0·3915	0·01088	0·3975	0·01102

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v.w.	444 K_β	0·424	0·00883	st.	532 611	0·414	0·01090	0·420	0·1103
v.w.	621 540 ?	0·4415	0·01077	w.	444 K_β	0·4295	0·00895	0·433	0·00903
v.w.	541	0·453	0·01078	v.w.	541			0·463	0·01101
v.w.	533	0·464	0·01079	m.	633 721 K_β	0·482	0·00893	0·487	0·00902
m.	633 721 K_β	0·476	0·00881	w.	631			0·505	0·01098
w.	631	0·4935	0·01073	st.	444	0·5215	0·01086	0·527	0·01097
m.	444	0·515	0·01073	m.	710 ? 550	0·543	0·01086	0·550	0·01100
w.	710 550 ?	0·537	0·01074	st.	633 721	0·5875	0·01088	0·595	0·01101
v.w.	641 720 ?	0·569	0·01074	w.	642			0·618	0·01102
st.	633 721	0·580	0·01074	st.	554 ? 741 811 ?	0·718	0·01088	0·726	0·0110
st.	554 ? 741 811 ?	0·709	0·01074	st.	644 ? 820	0·738	0·0108	0·750	0·0110
w.	644 ? 820	0·736	0·0108	m.	822 660	0·782	0·0109	0·792	0·0110
st.	822 660	0·7745	0·01076	m.	662			0·835	0·0110
w.	662	0·819	0·0107	m.	752			0·858	0·0110
				m.	840			0·884	0·0110
				w.	744 ?			0·893	0·0110
				m.	?			0·945	

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The values of the lattice parameters derived from the precision photograms are given in Table VI., together with the data necessary for determining the number of atoms per elementary cube.

TABLE VI.

Lattice Dimensions and Number of Atoms per Elementary Cube in the γ-Phases.

Alloy.	Per cent. Zn.	Average Atomic weight.	Density.	d_{100} in A.	Number of Atoms per elementary cube.
Cu–Zn ...	61·7	64·67	8·04	8·850	52·22
Cu–Zn ...	64·7	64·72	7·99	8·861	52·05
Cu–Zn ...	67·7	64·78	7·92	8·887	52·02
Ag–Zn ...	50·3	81·29	8·66	9·327	52·37
Au–Zn ...	36·9	113·07	12·25	9·268	52·27
Au–Zn ...	41·1	107·71	11·76	9·223	51·96

As might be gathered from the table, and also from the comparative precision photograms reproduced in fig. 6, II. (Pl. X.), the lattice dimensions of γ-brass increase in size with rising content of zinc. The lattice of γ-Au–Zn, however, becomes smaller the more zinc it contains. The lattice dimensions of the γ-phases change in the same way as they do in the α-phases, and corresponding to what might be expected if copper and gold atoms are replaced by zinc atoms one by one. The substitution seems to be *simple*. This is conclusively proved by the fact that exactly the same number of atoms per elementary cube, viz. 52, has been found in all the γ-phases investigated.

These 52 atoms cannot be structurally equivalent, and accordingly the γ-phase must be regarded as a solid solution in a chemical compound. It is impossible, however, to state definitely what formula this compound has, as long as nothing is known concerning the function of the atoms in the lattice. The only way of dividing the 52 atoms into two groups of structurally equivalent atoms is obviously in the proportion of 4 to 48. That leads up to formulæ of the types AB_{12} and $A_{12}B$, but such compounds can hardly be the bases of the γ-phases, as they fall far out of the composition range of the phases. The atoms within the elementary cube must thus be composed of at least three

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groups of structurally equivalent individuals. As there is a great number of combinations of that kind possible, and as it is unknown which of them corresponds to reality, it is impossible as the case now stands to find out the bases of the γ-phases.

By way of conjecture, the formulæ Cu_4Zn_9, Ag_4Zn_9, and Au_4Zn_9 may, however, possibly be suggested, as they correspond to compositions coinciding with one of the homogeneous γ-phase ranges *.

D. *The ϵ- and η-Phases.*

As all attempts to obtain a single crystal of any of the ϵ-phases failed, the determination of their structure had to be carried out by means of powder photograms only. Generally this procedure is not as reliable as the investigation of crystal individuals, but in this case there are very good reasons to believe that the results obtained are trustworthy.

The photograms were all very simple, and compared with the graphs of A. W. Hull and Wh. P. Davey †, they proved to be of the type corresponding to a close-packed hexagonal lattice, having an axial ratio of about 1·6. This confirms the statement of Owen and Preston concerning the structure of ϵ-brass. But as zinc and copper atoms differ very little in diffractive power, Owen and Preston were not able to decide if the two kinds of atoms in ϵ-brass were orientated in lattices of their own or if they were irregularly mixed in a common lattice; they considered it possible that the elementary parallelepiped of ϵ-brass actually was larger than indicated by the photogram. As, however, diffraction patterns of the ϵ-phases of the Ag–Zn and Au–Zn systems are quite like that of ϵ-brass, being both of the type corresponding to an element of close-packed hexagonal structure, it can hardly be doubted that the ϵ-phases are to be regarded as ideal solid solutions.

As might be expected, the η-phases were found to have the structure of zinc, being close-packed hexaxonal with an axial ratio of about 1·9. These phases must be considered to be solid solutions of copper, silver, and gold in zinc.

The lattice of the ϵ- and η-phases would thus be of the same kind, only differing as to their axial ratios. As is well known, the close-packed hexagonal elements may be divided into two groups, one having the axial ratio of about 1·9

* This is also the case with the γ'-phase of the Cu-Al systems, which accordingly would represent a solid solution in the compound Cu_9Al_4. Comp. Jette, Phragmén, and Westgren, *loc. cit.* p. 204.

† Phys. Rev. xvii. p. 549 (1921).

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(the Zn-type), and the other an axial ratio of about 1·6 (the Mg-type). When the atoms of a zinc lattice are substituted by copper, silver, or gold atoms to a sufficient extent, the lattice is thus changed from the first of these types to the other. As pointed out by Hull, the first of these lattices may be considered to be built up of atoms having the form of prolate spheroids and the other one may be regarded as formed of spheres or slightly flattened spheroids.

The $\sin^2\frac{\theta}{2}$ values obtained from precision photograms of the ϵ- and η-phases are given in Tables VII.–X. The

TABLE VII.

Precision Photograms of ϵ-Ag–Zn.

I obs.	I comp.	Radiation.	$h_1h_2h_3h_4$.	60·5 per cent. Zn.		78·1 per cent. Zn.	
				$\sin^2\frac{\theta}{2}$ obs.	$\sin^2\frac{\theta}{2}$ comp.	$\sin^2\frac{\theta}{2}$ obs.	$\sin^2\frac{\theta}{2}$ comp.
w.	...	K_β	$10\bar{1}0$	0·130	0·129	0·130	0·129
m.	...	K_β	0002	0·155	0·155	0·159	0·160
m.	3	K_α	$10\bar{1}0$	0·157	0·157	0·1565	0·157
m.	...	K_β	$10\bar{1}1$	0·168	0·168	0·169	0·169
st.	4	K_α	0002	0·189	0·188	0·194	0·195
st.	18	K_α	$10\bar{1}1$	0·204	0·204	0·206	0·206
w.	...	K_β	$10\bar{1}2$	0·2835	0·284	0·289	0·289
st.	6	K_α	$10\bar{1}2$	0·346	0·345	0·351	0·352
w.	...	K_β	$11\bar{2}0$	0·3865	0·387	0·388	0·388
st.	12	K_α	$11\bar{2}0$	0·470	0·471	0·471	0·472
m.	...	K_β	$10\bar{1}3$	0·477	0·477	0·488	0·489
w.	...	K_β	$11\bar{2}2$	0·541	0·542	0·546	0·548
v.w.	...	K_β	$20\bar{2}1$	0·554	0·555	0·5575	0·557
st.	18	K_α	$10\bar{1}3$	0·580	0·581	0·595	0·596
w.	3	K_α	$20\bar{2}0$	0·630	0·629	0·629	0·629
st.	24	K_α	$11\bar{2}2$	0·6595	0·659	0·6675	0·667
st.	18	K_α	$20\bar{2}1$	0·675	0·675	0·678	0·678
m.	4	K_α	0004	0·754	0·754	0·779	0·779
m.	6	K_α	$20\bar{2}2$	0·817	0·816	0·824	0·824
w.	...	K_β	$20\bar{2}3$	0·864	0·864	0·877	0·877
m.	6	K_α	$10\bar{1}4$	0·910	0·911	0·9365	0·937

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TABLE VIII.

Precision Photograms of ε-Brass.

I obs.	Radiation.	$h_1h_2h_3h_4$.	80·3 per cent. Zn.		86·1 per cent. Zn.	
			$\sin^2\frac{\theta}{2}$ obs.	$\sin^2\frac{\theta}{2}$ comp.	$\sin^2\frac{\theta}{2}$ obs.	$\sin^2\frac{\theta}{2}$ comp.
m.	K_β	$10\bar{1}2$	0·302	0·303	0·301	0·301
st.	K_α	$10\bar{1}2$	0·368	0·368	0·367	0·367
w.	K_β	$11\bar{2}0$	0·408	0·408	0·4025	0·403
st.	K_α	$11\bar{2}0$	0·4955	0·496	0·491	0·491
m.	K_β	$10\bar{1}3$	0·511	0·511	0·5105	0·510
w.	K_β	$11\bar{2}2$	0·576	0·575	0·570	0·570
v.w.	K_β	$20\bar{2}1$	0·5855	0·586	0·579	0·579
st.	K_α	$10\bar{1}3$	0·6215	0·622	0·6215	0·622
w.	K_α	$20\bar{2}0$	0·662	0·661	0·6555	0·655

TABLE IX.

Precision Photograms of ε-Au–Zn.

I obs.	Radiation.	$h_1h_2h_3h_4$.	67·5 per cent. Zn.		72·3 per cent. Zn.	
			$\sin^2\frac{\theta}{2}$ obs.	$\sin^2\frac{\theta}{2}$ comp.	$\sin^2\frac{\theta}{2}$ obs.	$\sin^2\frac{\theta}{2}$ comp.
m.	K_β	$10\bar{1}2$	0·289	0·290	0·290	0·291
st.	K_α	$10\bar{1}2$	0·353	0·353	0·353	0·354
w.	K_β	$11\bar{2}0$	0·389	0·389	0·389	0·389
st.	K_α	$11\bar{2}0$	0·474	0·474	0·474	0·474
w.	K_β	$10\bar{1}3$	0·490	0·490	0·4915	0·492
w.	K_β	$11\bar{2}2$	0·5495	0·549	0·5495	0·550
v.w.	K_β	$20\bar{2}1$	0·559	0·559	0·5585	0·559
st.	K_α	$10\bar{1}3$	0·5975	0·597	0·599	0·599
w.	K_α	$20\bar{2}0$	0·632	0·632	0·632	0·632
st.	K_α	$11\bar{2}2$	0·6695	0·669	0·6695	0·670
w.	K_α	$20\bar{2}1$	0·680	0·681	0·6805	0·681
	K_β	$20\bar{2}2$		0·679		0·680

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TABLE X.

Precision Photograms of Zinc, η-Brass, and η-Au–Zn.

I.	Radiation.	$h_1h_2h_3h_4$.	Zinc.		Au–Zn, 95·0 % Zn.		Cu–Zn, 96·5 % Zn.	
			$\sin^2\frac{\theta}{2}$ obs.	$\sin^2\frac{\theta}{2}$ comp.	$\sin^2\frac{\theta}{2}$ obs.	$\sin^2\frac{\theta}{2}$ comp.	$\sin^2\frac{\theta}{2}$ obs.	$\sin^2\frac{\theta}{2}$ comp.
m.	K_β	$10\bar{1}2$	0·271	0·271	0·273	0·273		
st.	K_α	$10\bar{1}2$	0·329	0·329	0·331	0·331		
w.	K_β	$10\bar{1}3$	0·428	0·428	0·432	0·430		
w.	K_β	$11\bar{2}0$	0·434	0·434		0·433		
st.	K_α	1013	0·520	0·521	0·525	0·523		
st.	K_α	$11\bar{2}0$	0·528	0·528		0·526		
w.	K_β	$11\bar{2}2$	0·560	0·560	0·559	0·559		
v.w.	K_β	$20\bar{2}0$	0·578	0·578				
w.	K_β	$20\bar{2}1$	0·610	0·610	0·606	0·605		
st.	K_α	$11\bar{2}2$	0·681	0·681	0·680	0·680	0·6815	**0·681**
w.	K_α	$20\bar{2}0$	0·704	0·704	0·697	0·697	0·7015	**0·702**
st.	K_α	$20\bar{2}1$	0·742	0·742	0·737	0·736	0·740	**0·740**
w.	K_α	$10\bar{1}4$	0·789	0·789	0·801	0·802		
st.	K_α	$20\bar{2}2$	0·858	0·858	0·854	0·854	0·856	**0·856**

values of the intensity $J_{comp.}$, given in Table VII., are deduced from the product of the relative occurrence of the reflecting planes and the factor of structure.

In fig. 6, III. (Pl. X.) comparative photograms are reproduced of two Ag–Zn alloys, one containing 60·5 per cent. Zn, and the other 78·1 per cent. Zn. It may be seen in this figure how the interferences of these hexagonal substances are displaced unequally when the composition of the phase is changed.

The lattice dimensions vary as the zinc is substituted by silver, but the two parameters of the lattice are not altered in the same proportion. In spite of this considerable and unequal change in the $\sin^2\frac{\theta}{2}$ values with varying composition, the diffraction angles of the different ϵ-phases always satisfy

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an equation of the type corresponding to a hexagonal lattice:

$$\sin^2\frac{\theta}{2} = \frac{\lambda^2}{3a_1^2}(h_1^2+h_1h_2+h_2^2) + \frac{\lambda^2}{4a_4^2}h_4^2.$$

where λ is the wave-length, and a_1 and a_4 are the side and height respectively of the elementary prism.

This perfect agreement forms the most important support for the conception that the ϵ-phases have a hexagonal structure.

The intensity values observed agree with those computed for a close-packed hexagonal lattice, with the exception that for some of the alloys the reflexions against the basal planes show up a little stronger than expected. This is probably due to the fact that the grains of the alloys at the powdering have been pressed into thin lamellæ, the largest faces of which are parallel to the basal planes. Thus the crystal individuals have not been orientated completely at haphazard in the specimens investigated, but a disproportional number of them have got an orientation parallel to the axis of the rod, or to the surface illuminated.

The density values and the final X-ray data of the ϵ- and η-phases are included in Table XI. In the close-packed hexagonal lattice there should be two atoms in the elementary parallelepiped, and within the limits of error this number has in fact been obtained for all the phases investigated. It may be noted in the table mentioned that in all the phases the axial ratio $\frac{a_4}{a_1}$ is approaching towards 1·63 with increasing content of copper, silver, or gold—*i. e.*, the more atoms of the latter kind the lattice contains, the more it gets the shape of one built up of spherical atoms.

E. *The γ'- and γ''-Phases of the* Au–Zn *System.*

From powder photograms of the Au–Zn alloys in the range 49–55 per cent. zinc it could be concluded that two phases existed in that range to which no analogies were found in the Cu–Zn and Ag–Zn systems. One of these phases, called γ', is stable at ordinary temperature, and is homogeneous within a composition range range of only 1 per cent. at about 50 per cent. zinc. The other, γ'', was found to be stable only at higher temperatures. Alloys containing 53 to 55 per cent. zinc consisted of the three phases γ', γ'', and ϵ. A gold-zinc melting with 53·5 per cent. zinc quenched in water from the liquid state gave a photogram (Pl. IX. fig. 5, VI.) where the γ''-interferences predominate.

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Table XI.

Lattice Dimensions and Number of Atoms per Elementary Parallelepiped in the ϵ- and η-Phases.

Phase.	Per cent. Zn.	Average Atomic Weight.	Density.	$\frac{\lambda^2}{3a_1^2}$.		$\frac{\lambda^2}{4a_1^2}$.		a_1 in Å.	a_1 in Å.	$\frac{a_1}{a_1}$.	V in Å^3.	Number of Atoms per Elementary Parallelepiped.
				K_α.	K_β.	K_α.	K_β.					
Cu–Zn	80·3	65·01	7·71	0·1652	0·1360	0·0507	0·0417	2·746	4·294	1·564	28·04	2·01
Cu–Zn	86·1	65·11	7·51	0·1637	0·1342	0·0509	0·0418	2·761	4·286	1·552	28·30	1·98
Ag–Zn	60·5	77·42	8·35	0·1570	0·1290	0·0471	0·0387	2·818	4·456	1·581	30·64	2·00
Ag–Zn	78·1	71·54	7·77	0·1573	0·1292	0·0487	0·0400	2·815	4·382	1·557	30·07	1·98
Au–Zn	67·5	83·52	9·34	0·1580	0·1297	0·0488	0·0400	2·809	4·377	1·558	29·91	2·03
Au–Zn	72·3	80·23	8·67	0·1580	0·1297	0·0490	0·0402	2·809	4·369	1·555	29·86	1·96
Cu–Zn	96·5	65·31	7·26	0·1754	...	0·0387	...	2·666	4·916	1·844	30·26	2·04 †
Au–Zn	95·0	67·63	7·40	0·1743	0·1432	0·0392	0·0322	2·674	4·887	1·828	30·27	2·01
Zn	100·0	65·37	7·14 *	0·1760	0·1446	0·0383	0·0315	2·662	4·941	1·856	30·31	2·01

* A. C. Egerton and W. B. Lee, Proc. Roy. Soc. A, ciii. p. 499 (1923).

† The divergence of this value from 2·00, the one expected, is probably due to the fact that this alloy does not consist of pure η but also contains some ϵ.

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When the same specimen was investigated only one day after quenching, the interferences corresponding to γ' and ϵ had already become considerably more distinct, which may be seen in the precison photograms VIII. to X. in fig. 5 (Pl. IX.). It is thus evident that γ'' splits up spontaneously into γ' and ϵ at the ordinary temperature.

The γ''-phase could never be obtained quite free from the adjacent phases, and, unfortunately, all attempts failed to get a single crystal of γ'. The investigation had thus to be confined to the powder method only. Some of the photograms obtained are shown in fig. 5 (Pl. IX.).

As may be seen in Table XII., the γ'-interferences are in accordance with the formulæ:

$$\sin^2\frac{\theta}{2} = 0{\cdot}01506\,(h_1^2 + h_2^2 + h_3^2) \;\ldots\; (\mathrm{K}_\alpha),$$

$$\sin^2\frac{\theta}{2} = 0{\cdot}01238\,(h_1^2 + h_2^2 + h_3^2) \;\ldots\; (\mathrm{K}_\beta).$$

As every line of the photogram agrees perfectly with these formulæ, it is highly probable that they really represent the correct quadratic forms of the γ'-phase. The γ'-crystals would thus be cubic with a parameter of 7·880 Å.

Density measurements on three γ'-alloys containing 48·3, 50·2, and 50·5 per cent. zinc gave the values 10·88, 10·63, and 10·56 respectively. Of these specimens the one containing 50·2 per cent. zinc consisted of only γ', while the first was a mixture of γ' with some γ, and the third contained some γ'' beside γ'. The average weight of the atoms in the homogeneous γ'-specimen was calculated to $98{\cdot}1 \,.\, 1{\cdot}650 \times 10^{-24}$ gm., and consequently the number of atoms per elementary cube in that phase would be 32·17, *i. e.* 32 within the limit of error. As the homogeneous γ'-phase contains 75 atomic per cent. zinc, its elementary cube would thus be occupied by 8 gold and 24 zinc atoms, and there is accordingly nothing contradicting the statement of Saldau, that the phase consists of $AuZn_3$.

As may be seen in fig. 5 (Pl. IX.), the photograms of the quenched alloy containing 53·5 per cent. zinc (VI. and VIII.) are not quite free from interferences corresponding to the γ'-phase (V. and X.). Yet a striking resemblance between photogram VI. and the γ-photogram (VII.) may be noted. In fact, at a hasty glance these diffraction patterns seem to be identical. A closer inspection shows, however, that there is a distinct difference between them. The $\sin^2\frac{\theta}{2}$ values of the five strongest interferences are in both photograms in the

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TABLE XII.—Powder Photogram of γ-Au–Zn (50·2 per cent. Zn).

I.	Radiation.	$h_1^2+h_2^2+h_3^2$.	$\sin^2\frac{\theta}{2}$.	$\frac{\sin^2\frac{\theta}{2}}{h_1^2+h_2^2+h_3^2}$.	I.	Radiation.	$h_1^2+h_2^2+h_3^2$.	$\sin^2\frac{\theta}{2}$.	$\frac{\sin^2\frac{\theta}{2}}{h_1^2+h_2^2+h_3^2}$.
v.w.	K_β	4	0·050	0·0125	v.w.	K_β	34	0·4215	0·01240
w.	K_α	4	0·060	0·0150	st.	K_α	29	0·437	0·01507
m.	K_α	5	0·075	0·0150	w.	K_α	30	0·451	0·01503
m.	K_α	6	0·0905	0·01508	v.w.	K_β	38	0·471	0·01239
w.	K_α	8	0·1205	0·01506	m.	K_α	32	0·483	0·01509
w.	K_β	13	0·160	0·01231	m.	K_α	34	0·512	0·01506
w.	K_β	14	0·173	0·01236	v.w.	K_α	35	0·528	0·01508
st.	K_α	13	0·1955	0·01504	m.	K_α	36	0·542	0·01506
st.	K_α	14	0·211	0·01507	w.	K_α	37	0·558	0·01505
m.	K_α	16	0·241	0·01506	st.	K_α	38	0·573	0·01505
w.	K_α	17	0·2565	0·01509	w.	K_α	41	0·6175	0·01506
v.w.	K_β	21	0·259	0·01233	w.	K_α	42	0·645	0·01504
w.	K_α	18	0·2715	0·01508	m.	K_α	44	0·664	0·01509
v.w.	K_α	19	0·286	0·01505	m.	K_α	45	0·6775	0·01506
w.	K_α	20	0·301	0·01505	m.	K_α	46	0·692	0·01504
m.	K_α	21	0·3165	0·01507	w.	K_α	49	0·737	0·01504
m.	K_α	22	0·332	0·01509	m.	K_α	52	0·782	0·01504
m.	K_β	29	0·361	0·01241	st.	K_α	53	0·797	0·01504
v.w.	K_α	25	0·377	0·01508	m.	K_α	54	0·814	0·01508
w.	K_β	32	0·396	0·01237	st.	K_α	61	0·918	0·01505

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proportion 3, 6, 9, 11, and 12; but there are some lines corresponding to the γ''-phase which are incompatible with the quadratic formula of the γ-phase. Among these are the least deviated interferences, which give the $\sin^2\frac{\theta}{2}$ values 0·068 and 0·083. If the γ''-phase is cubic, which seems most probable in view of the simple relation between the $\sin^2\frac{\theta}{2}$ values of its strongest lines, the constant of its quadratic form must thus be equal to or less than 0·083–0·068, *i. e.* 0·015. In fact, half of this value, *i. e.* 0·0075, gives a suitable constant. Every K_α-interference of γ'' can be explained by the formula:

$$\sin^2\frac{\theta}{2} = 0{\cdot}0075\,(h_1^2 + h_2^2 + h_3^2).$$

The $(h_1^2 + h_2^2 + h_3^2)$ values of the five strongest lines would accordingly be 27, 54, 81, 99, and 108. The formula gives a lattice parameter of 11·17 Å.; and, as the density of the alloy was found to be 10·2, there would thus be about 90 atoms in its elementary cube. As the specimen investigated was not homogeneous, the results of the X-ray investigation must, however, in this case be considered to be somewhat uncertain *.

According to Saldau †, $AuZn_3$ should be subjected to transformations in the solid state. An attempt was made to test if an alloy of that composition really solidifies in some other form than γ'. For this purpose it was quenched in water from a temperature above its melting-point, by which procedure at least some part of the phases stable at higher temperatures might be expected to be retained. The photogram of this product was, however, completely identical with a γ'-photogram; no new interferences whatever appeared. The negative result of this experiment cannot, however, be considered to settle the question, as eventual transformations may very well be complete, even at a most rapid quenching ‡.

* The authors have recently commenced an analysis of the Au-Cd system, and have found that an Au Cd alloy containing somewhat more than 75 atomic per cent. Cd gives a powder photogram which is similar to that of γ''-Au-Zn. It seems, thus, as if the Au-Cd system should have a phase that is analogous to γ''-Au-Zn, but stable at ordinary temperature. A closer investigation of this phase will, perhaps, throw some light also upon γ''-Au-Zn.

† *Loc. cit.*

‡ Comp. note on p. 320.

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6. Concluding Remarks.

At a general survey of the results of the X-ray analysis, it might seem as if in some cases the chemical characterization of metallic phases could not be performed much more definitely by this new procedure than has been possible by previous methods. When it cannot be settled if chemically identical atoms of a metallic phase are structurally equivalent or not, a chemical formula can at the utmost be suggested with a certain degree of probability; its validity is not to be conclusively proved.

From the fact that the ordinary valency rules do not hold for intermetallic compounds, it follows, however, that the chemical constitution of these substances is not defined by their chemical formulæ to the same extent as is, for instance, the case with electrolytes or gaseous compounds. Even if it were possible to find out the correct formulæ for the bases of metallic phases, it would certainly not bring about any deeper insight into the question of intermetallic reactivity.

The X-ray analysis makes, however, a penetration of this problem possible. Chemically related phases give photograms of a similar type; and even if these photograms sometimes cannot be completely unravelled, they prove in an incontrovertible way the relationship between different phases and display analogies between different metallic systems.

What, however, makes this X-ray research of alloys seem most promising is the fact that some types of structure seem to recur frequently in the metallic systems. Thus the atomic arrangements of the β- and γ-phases, described above, seem to be common; and in a preliminary investigation of the Ag–Cd, Ag–Al, Cu–Sn, and Ag–Sn systems the authors have got photograms indicating that in all these alloys a phase is present which has the same structure as the ϵ-phase of the Cu–Zn, Ag–Zn, and Au–Zn alloys*.

X-ray research will therefore undoubtedly, to a very high degree, contribute to the unveiling of the laws governing the combination of the atoms in composite metallic phases.

7. Summary.

1. According to the authors' opinion, the difference between solid chemical compounds and solid solutions lies in their structure. The terms *ideal solid chemical compound* and *ideal solid solution* are defined, and it is pointed out that most of the metallic phases represent intermediate stages between these two extreme types of structure.

* Comp. *Zsigmondy-Festschrift, Erg.-Band der Kolloid-Zeitschr.* xxxvi. p. 86 (1925).

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2. X-ray analysis of the Cu–Zn, Ag–Zn, and Au–Zn systems has proved that the five different types of structure occurring in the first-mentioned of these systems are met with also in the other ones. In addition to them there are two more phases found in the Au–Zn-system.

The β- and γ-phases of the Cu–Zn system have been investigated in the form of single crystals; in other cases the analyses have been performed by means of the powder method only. Arranged according to rising content of zinc, the structures common to the three systems have turned out to be the following:—α, face-centred cubic; β, cubic of CsCl-type; γ, cubic with 52 atoms in the elementary cube; ϵ, close-packed hexagonal with an axial ratio of 1·55–1·60; and η, close-packed hexagonal with an axial ratio of 1·80–1·90. An Au-Zn phase (γ') containing about 50 per cent. Zn was found to be cubic, very likely with an elementary cube occupied by 32 atoms; another phase (γ''), obtained by quenching Au–Zn alloys containing 53–54 per cent. Zn, seemed also to be cubic, with about 90 atoms in its elementary cube. The powder photogram of the γ''-phase has a peculiar similarity to those of the γ-phases.

3. In accordance with the definitions made, the α-, η-, and, with great probability, also the ϵ-phases represent ideal solid solutions, the first one having Cu, Ag, or Au, and the last two Zn, as solvent. The other phases may be regarded as solid solutions in chemical compounds. The solvents of the β-phases are CuZn, AgZn and AuZn. By way of conjecture the formulæ Cu_4Zn_9, Ag_4Zn_9, and Au_4Zn_9 are proposed for the bases of the γ-phases, and it is most likely that the γ-phase of the Au–Zn system corresponds to $AuZn_3$.

The Metallographic Institute, Stockholm,
February 1925.

XXXII. *Optical Interference Experiments with Multiple Sources.* *By* JOHN J. DOWLING, *M.A., F.Inst.P., M.R.I.A., and* J. A. C. TEEGAN, *M.Sc.**

[Plate XII.]

WITH the possible exception of the Lummer parallel plate interferometer, there does not appear to have been any attempt made to extend the investigation of the class of interference phenomena associated with the names of Young, Fresnel, and Lloyd to the cases where there are more than two sources. The ordinary diffraction grating may be considered as equivalent to a large number of equally-spaced

* Communicated by the Authors.

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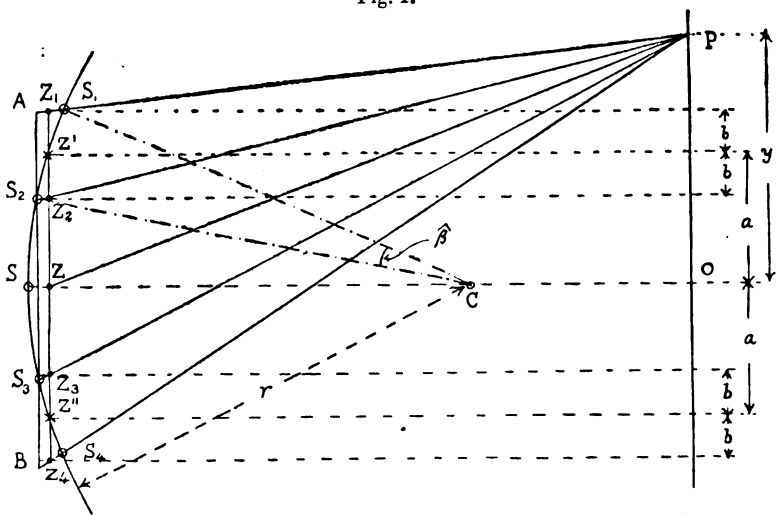
sources; but it seems of interest to describe briefly some results we have been able to obtain with an arrangement giving four (and eight) coherent sources grouped in any desired symmetrical arrangement.

A brief statement of the theory may be stated thus:—

The light proceeding from a source Z (fig. 1) arriving at P yields a vibration

$$z = A \sin \frac{2\pi}{\lambda}\left[Vt - x - \frac{y^2}{2x}\right] \quad . \quad . \quad . \quad . \quad . \quad \text{(I.)}$$

Fig. 1.



If Z be divided (*e.g.* by a biprism) into two coherent sources Z′ and Z″ (2*a* apart),

$$z = \frac{A}{2} \sin \frac{2\pi}{\lambda}\left[Vt - x - \frac{(y+a)^2}{2x}\right]$$
$$+ \frac{A}{2} \sin \frac{2\pi}{\lambda}\left[Vt - x - \frac{(y-a)^2}{2x}\right]$$
$$\doteqdot A \cos \frac{2\pi}{\lambda}\left[\frac{ay}{x}\right] . \sin \frac{2\pi}{\lambda}[Vt - x]. \quad . \quad . \quad . \quad \text{(II.)}$$

A further division of Z′ and Z″ each into two sources (2*b* apart) yields four sources, Z_1, Z_2, Z_3, Z_4, arranged along the line Z_1, Z, Z_4 at $a+b$; $a-b$; $-a+b$; $-a-b$. The vibration at P is

$$z = \Sigma \frac{A}{4} \sin \frac{2\pi}{\lambda}\left[Vt - x - \frac{(y \pm a \pm b)^2}{2x}\right]$$
$$\doteqdot A \cos\left(\frac{2\pi}{\lambda} \cdot \frac{ay}{x}\right) . \cos\left(\frac{2\pi}{\lambda} \cdot \frac{by}{x}\right) . \sin \frac{2\pi}{\lambda}(Vt - x). \quad \text{(III.)}$$

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The separations a and b are effected by two biprisms, one mounted behind the other in front of the slit. If α, β are the acute angles of these biprisms, and R and r their respective distances from the slit,

$$a \doteqdot (\mu-1)\alpha R, \quad \text{and} \quad b \doteqdot (\mu-1)\beta r. \quad . \quad \text{(IV.)}$$

The grouping is symmetrical, but the most interesting case is when $b=2a$ (or $a=2b$), the four sources being then equally spaced. Here

$$z=\left\{\frac{A \sin 4\left(\frac{2\pi}{\lambda}\cdot\frac{ay}{x}\right)}{4 \sin\left(\frac{2\pi}{\lambda}\cdot\frac{ay}{x}\right)}\right\} \sin\frac{2\pi}{\lambda}(Vt-x). \quad . \quad . \quad \text{(V.)}$$

The illumination distribution, proportional to the square of the term in chain brackets, corresponds to that of a grating having four openings.

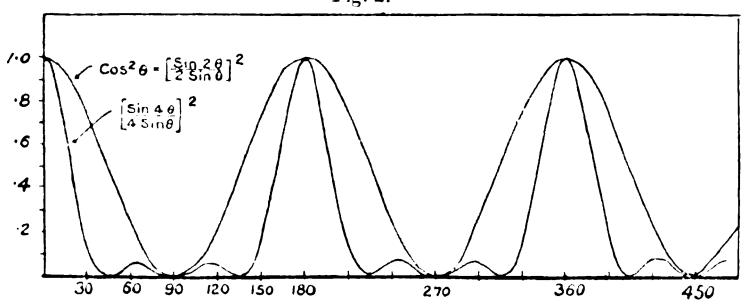
A further subdivision may now be carried out, using a third biprism; and if the spacing constant $2c=4b=8a$, we again arrive at the corresponding grating distribution.

The illumination, as a function of

$$\theta=\frac{2\pi}{\lambda}\cdot\frac{ay}{x},$$

is shown in fig. 2. The upper curve shows the illumination

Fig. 2.



of the fringes due to two sources (Fresnel's experiment): the lower curve with subsidiary maxima that due to four equally-spaced sources (two biprisms). In Pl. XII. enlarged photographs of the fringes are given: A, with the first biprism alone; B, with the second; C, with both biprisms in position. The characteristic narrowing and intensification of the principal maxima are clearly observable in the part of the field indicated by the arrow.

It was found extremely difficult to locate the fringe

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systems when three biprisms were installed, so much so that we were unable to get a good photograph. The following considerations afford a clue to why this should be.

Reverting to fig. 1, it will be observed that the four sources, S_1, S_2, S_3, S_4, are actually situated around a circle of radius r, the distance of the second biprism from the slit S. Let us reconsider the formula for four equispaced sources in this connexion. Let x be now measured from the plane $A S_2 S_3 B$ a little in front of S. It will be readily found that, since $b=2a$,

$$\xi = Z_1S_1 + Z_2S_2 \doteqdot \frac{4a^2}{r} \quad . \quad . \quad . \quad . \quad . \quad \text{(VI.)}$$

We must now write, instead of equations (III.),

$$z = \Sigma_2 \frac{A}{4} \sin \frac{2\pi}{\lambda} \left\{ Vt - x - \frac{[y \pm (a-b)]^2}{2x} \right\}$$
$$+ \Sigma^2 \frac{A}{4} \sin \frac{2\pi}{\lambda} \left\{ Vt - x - \xi - \frac{[y \pm (a+b)]^2}{2x} \right\}$$
$$\doteqdot \frac{A}{2} \cos \frac{2\pi}{\lambda} \frac{y(a-b)}{x} \sin \frac{2\pi}{\lambda} (Vt - x)$$
$$+ \frac{A}{2} \cos \frac{2\pi}{\lambda} \frac{y(a+b)}{x} \cdot \sin \frac{2\pi}{\lambda} (Vt - x - \xi).$$
$$. \quad . \quad . \quad . \quad . \quad . \quad \text{(VII.)}$$

This will only reduce to the final form of (III.) when $\xi = \frac{n\lambda}{2}$, and we may regard ξ as affecting the "visibility" of the fringes. The value of ξ* depends on the position of the second biprism, and we found that the "visibility" underwent rapid variations with small displacements of that biprism in the neighbourhood of the position which made $b=2a$. It was indeed possible, but by no means easy, to obtain visual fringes of the proper type, using three biprisms; but we were unable to obtain a photograph, for the reason that the fringes were localized in a very restricted space, rendering very accurate registration of the photographic plate essential.

* Numerical data:—

Angular separation by second biprism

$= 30' = \frac{\pi}{360}$, $r = 32{\cdot}3$ cms. $\quad 4a = 2b = \frac{\pi r}{360} \doteqdot {\cdot}3$ cm.

$\xi = \frac{4a^2}{r} \doteqdot 70 \times 10^{-5}$. $\quad \lambda \doteqdot 5000 \times 10^{-8}$ cm.

Hence $n \doteqdot 28$.

[*The Editors do not hold themselves responsible for the views expressed by their correspondents.*]

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FIG. 11.

Grid Condenser Rectification Curve.

FIG. 12.

Alternator Voltage (instrument uncompensated).

FIG. 13.

Alternator Voltage (instrument compensated).

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[*The Editors do not hold themselves responsible for the views expressed by their correspondents.*]

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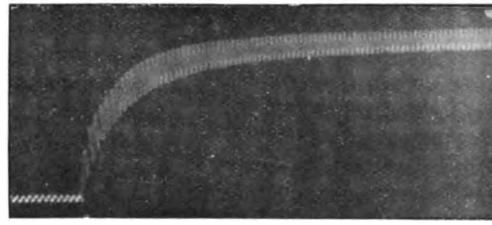
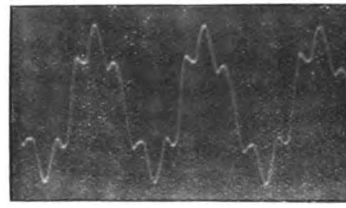
FIG. 11.



Grid Condenser Rectification Curve.

FIG. 12.



Alternator Voltage (instrument uncompensated).

FIG. 13.

Alternator Voltage (instrument compensated).

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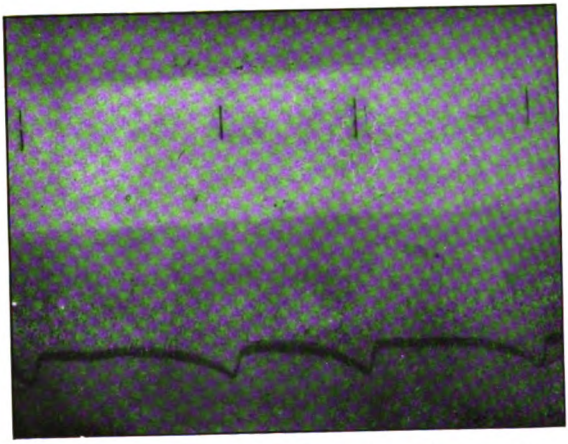
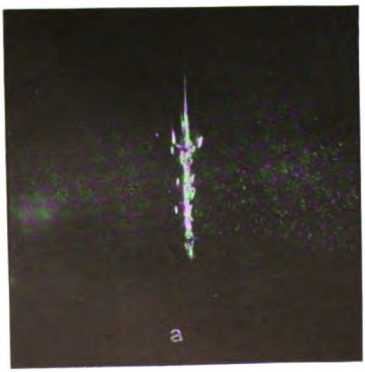
FIG. 1.



Showing coincidence between luminosity at the point (above) and interruption of the current.

FIG. 4.



Appearance of point: *a* during normal stage; *b* during highly resistant stage.

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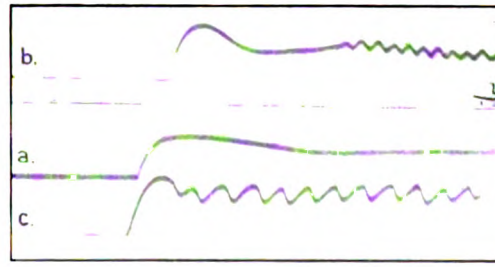
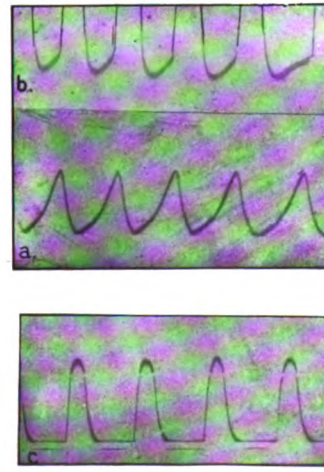
FIG. 5.



Oscillograms of current through break. *a*, below critical voltage. *b*, just above critical voltage. *c*, as in *b* with $\frac{1}{10}$ m.h. self-induction.

FIG. 6.



Oscillograms of normal interruptions. *a*, current graph. *b*, potential graph (through 2000 ohms). *c*, potential graph (through 10,000 ohms).

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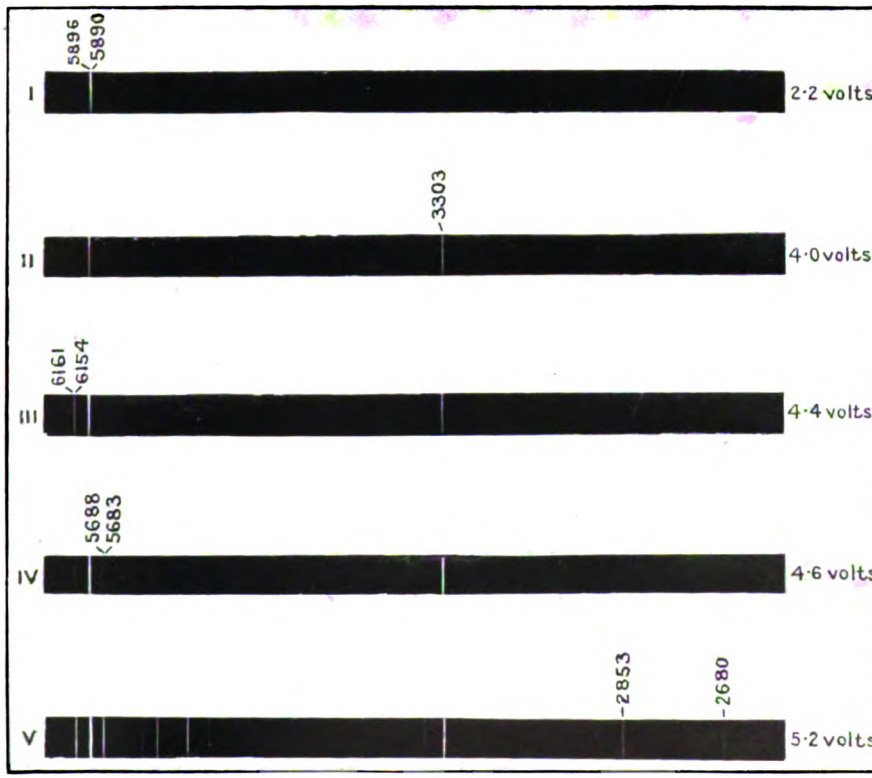

The Spectrum of Sodium at Low Voltages.

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FIG. 1.

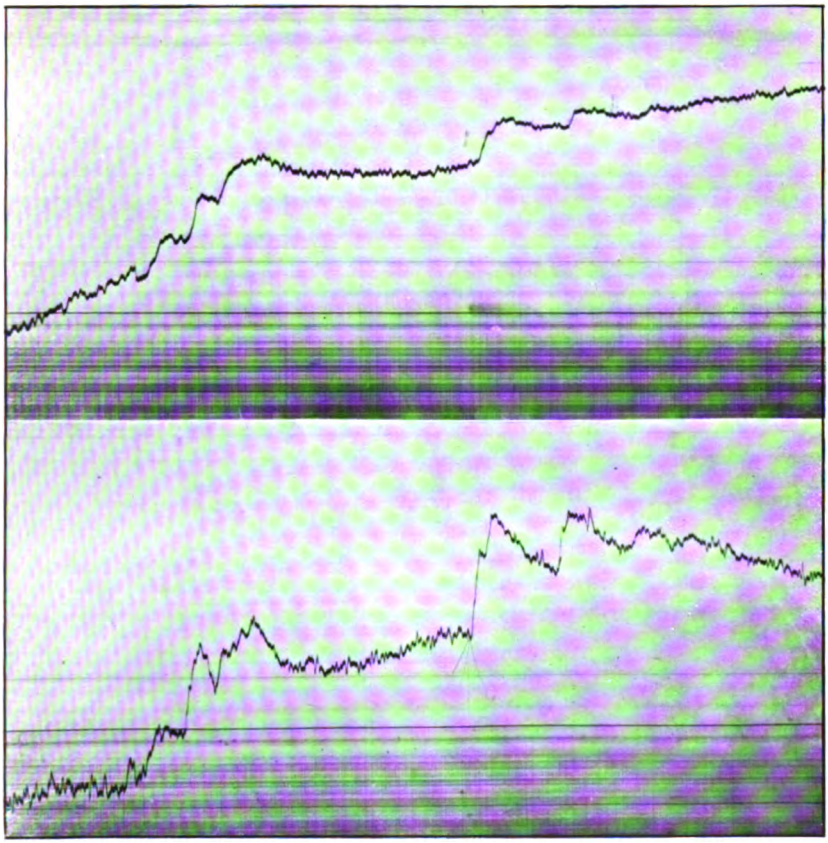
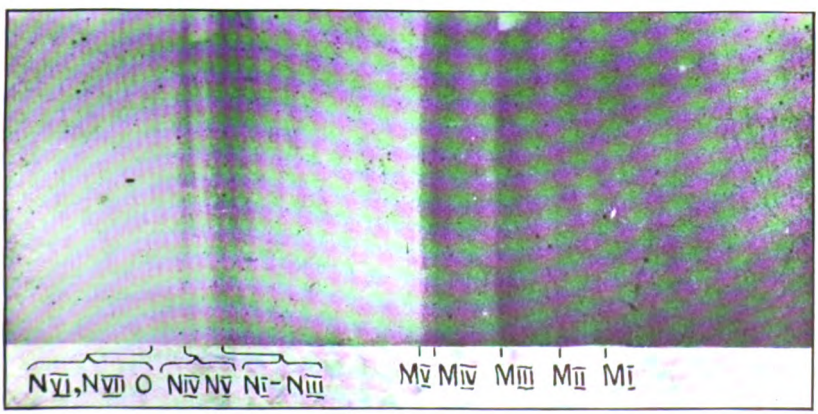


FIG. 2.



GOLD TARGET. 49·4 Gauss.

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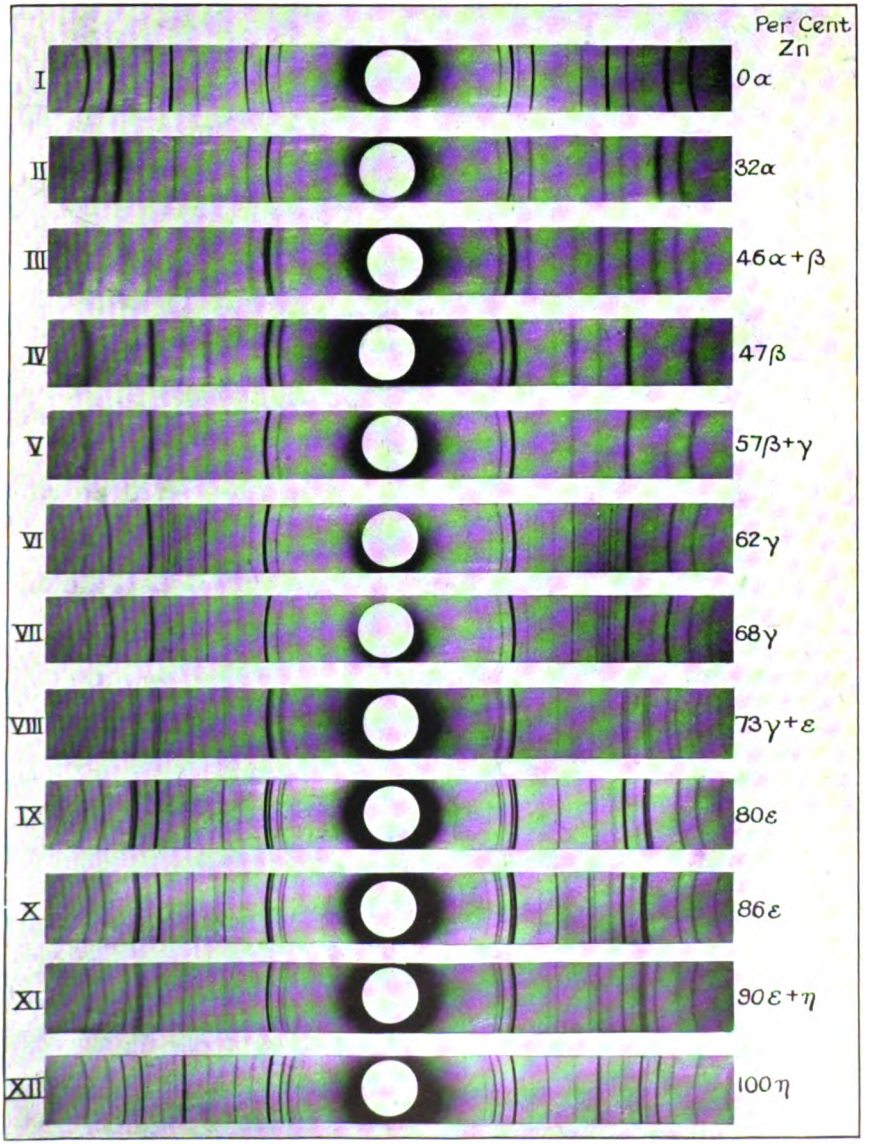
FIG. 2.



POWDER PHOTOGRAMS OF COPPER-ZINC ALLOYS.

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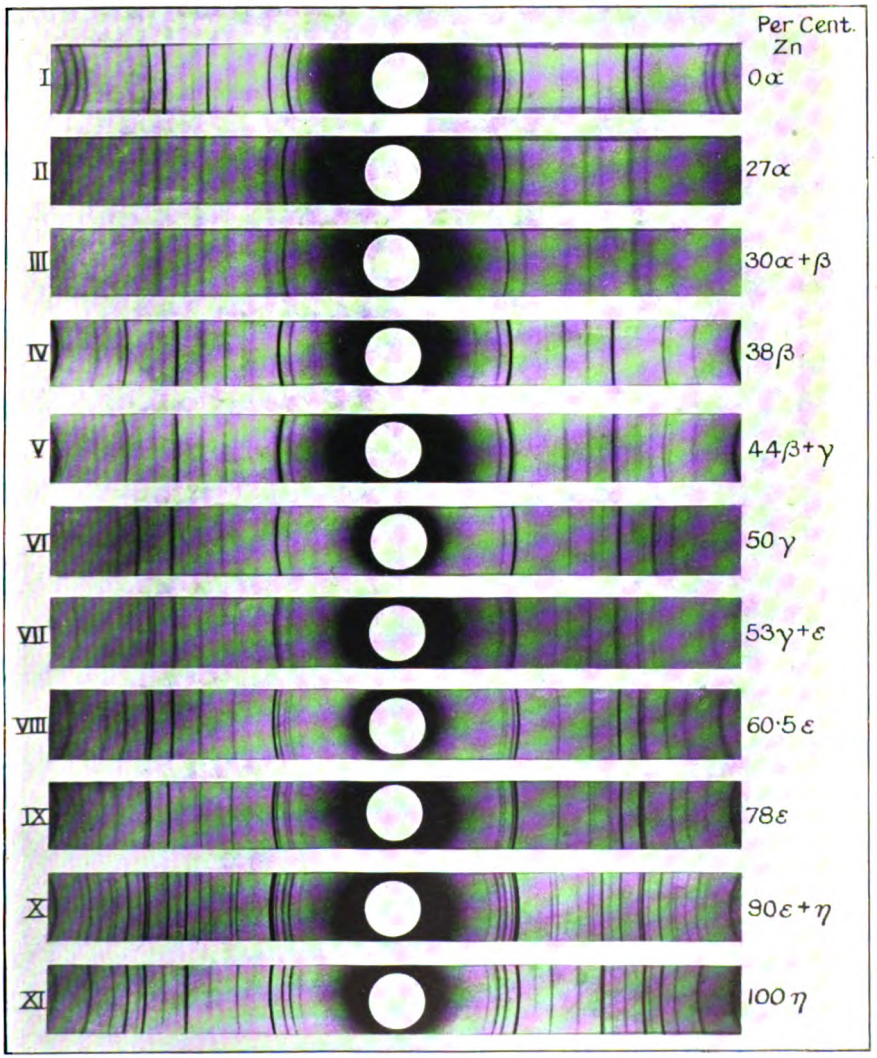
FIG. 3.



POWDER PHOTOGRAMS OF SILVER-ZINC ALLOYS.

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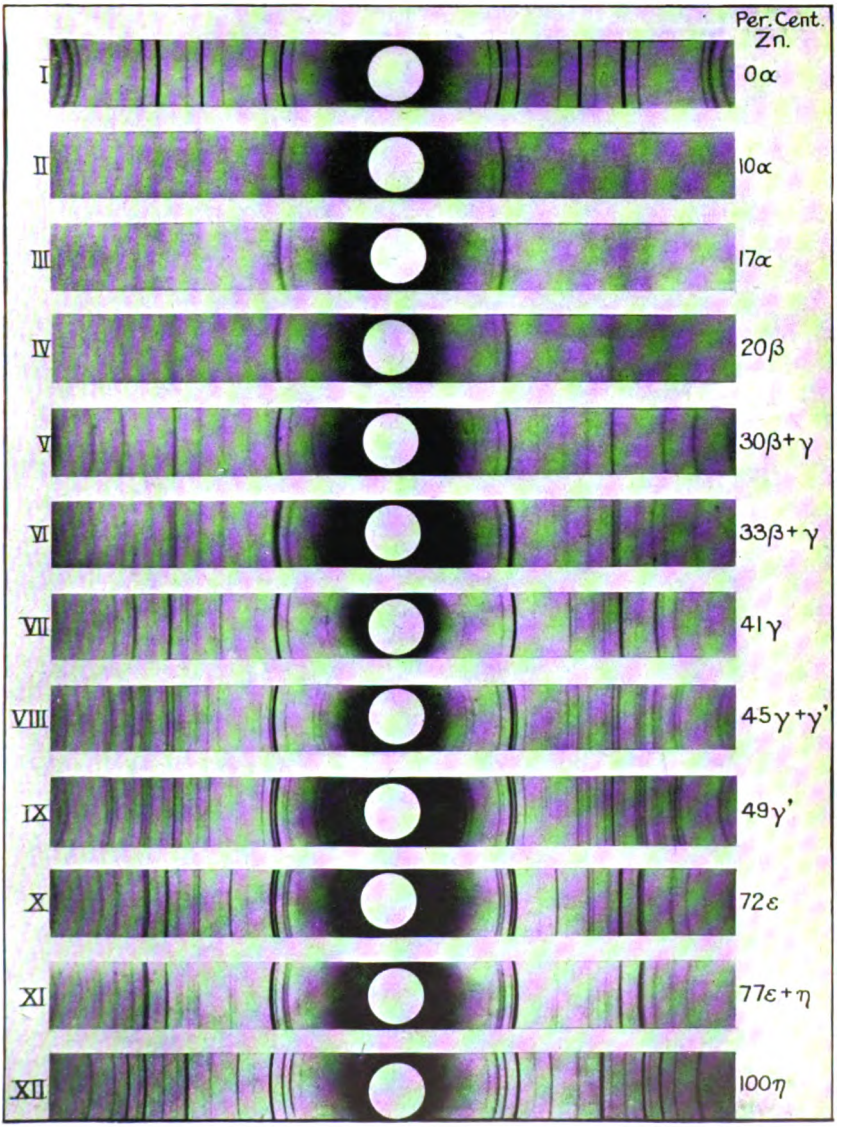
FIG. 4.



POWDER PHOTOGRAMS OF GOLD-ZINC ALLOYS.

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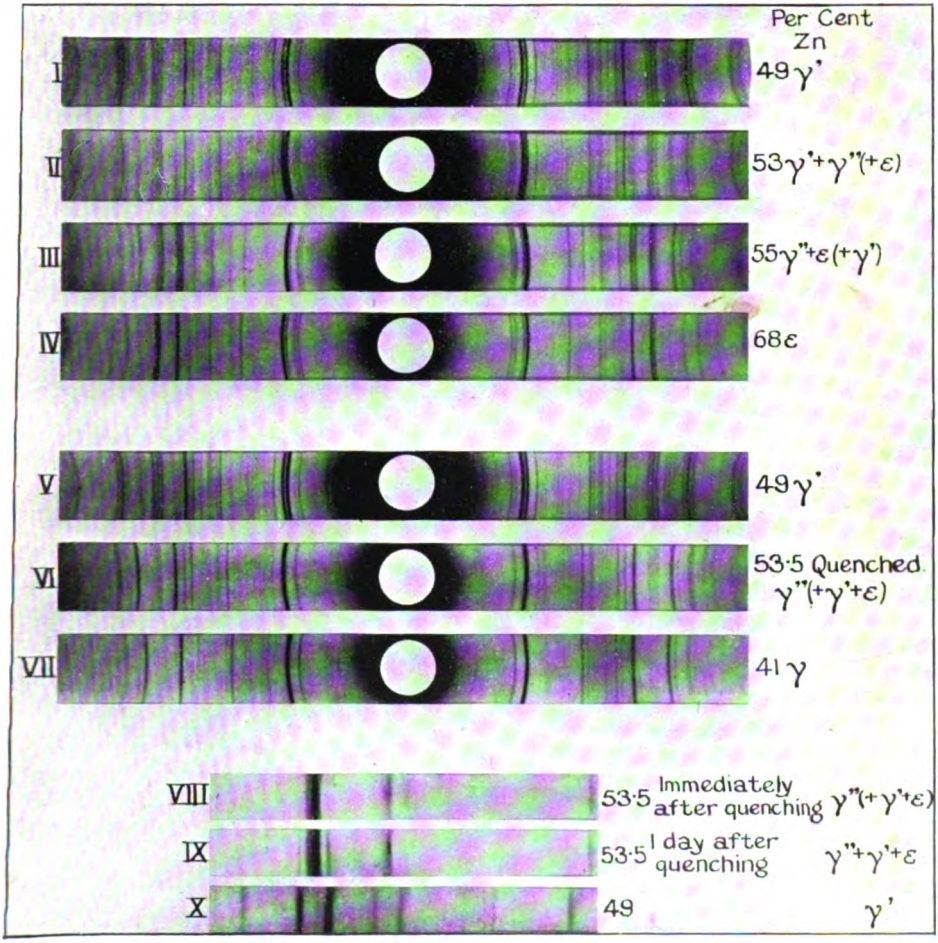
FIG. 5.



POWDER PHOTOGRAMS OF GOLD-ZINC ALLOYS (41–68 per cent. Zn).

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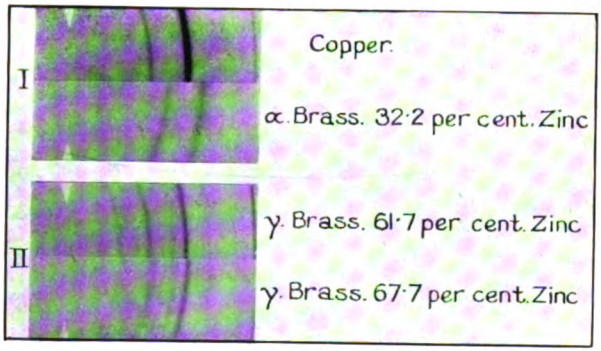
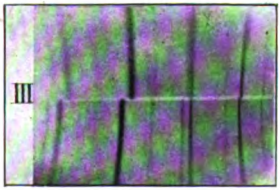
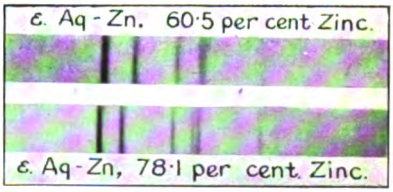
FIG. 6.







COMPARATIVE PRECISION PHOTOGRAMS.

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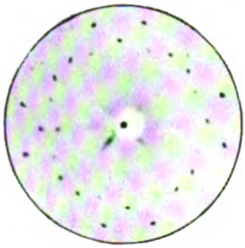
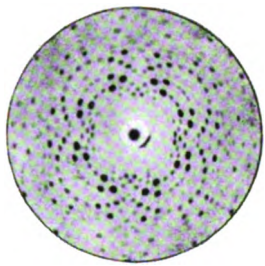
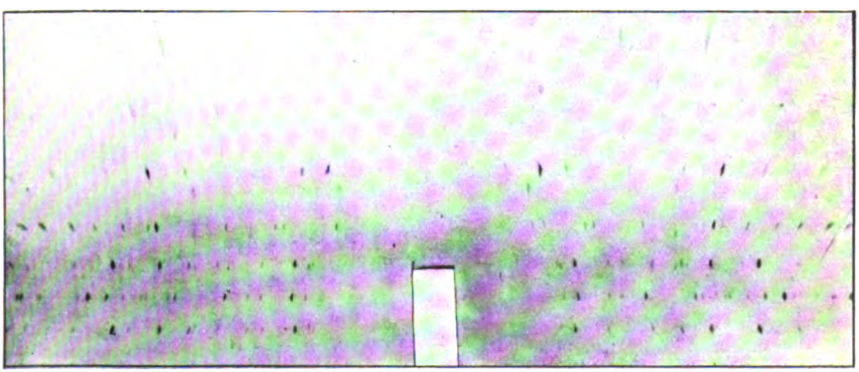
FIG. 7.



I. Laue Photogram of β-Brass.
Projection Distance 4·33 centimetres.
$\lambda > 0{\cdot}16$ Å.
Reduced 3 : 5.



II. Laue Photogram of γ-Brass.
Projection Distance 4·45 centimetres.
$\lambda > 0{\cdot}16$ Å.
Reduced 3 : 5.



III. Photogram of a γ-Brass Crystal rotating around [100].
Diameter of Film Cylinder 6·3 centimetres.
Reduced 3 : 5.

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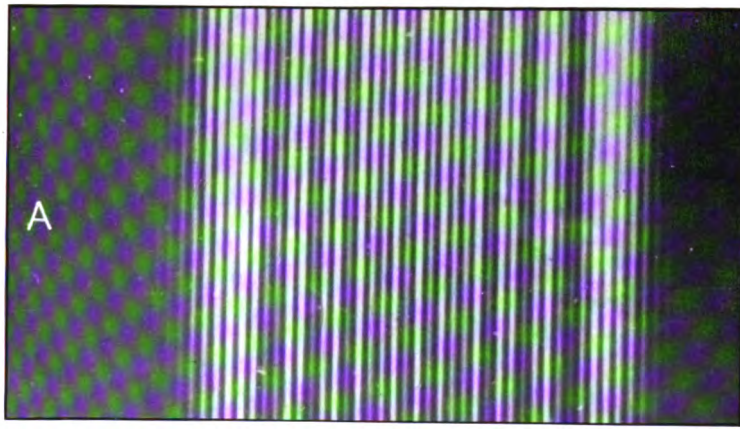

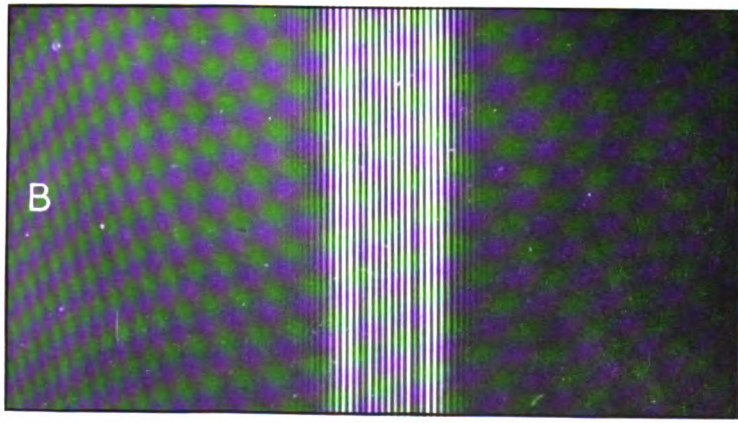

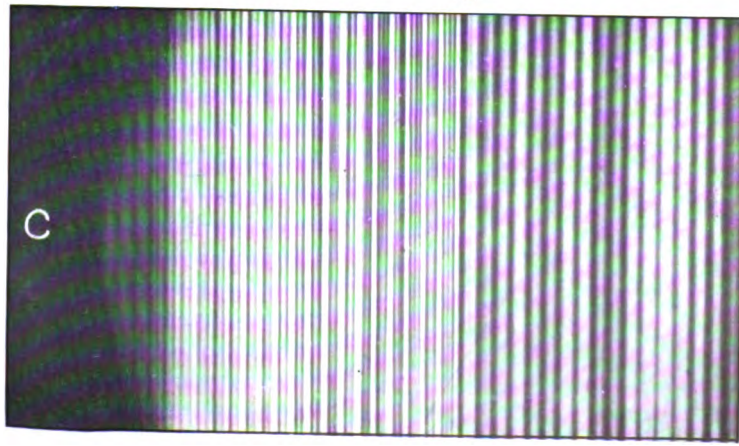

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THE

LONDON, EDINBURGH, AND DUBLIN

PHILOSOPHICAL MAGAZINE

AND

JOURNAL OF SCIENCE.

[SIXTH SERIES.]

AUGUST 1925.

XXXIII. *The Photoelectric Effect in Potassium Vapour as a Function of the Frequency of the Light.* By ERNEST ORLANDO LAWRENCE*, *M.A., Sloane Fellow in Physics, Yale University*†.

Introduction.

BECAUSE of our ignorance of the precise nature of the ejection of electrons by light from solid surfaces, that is to say, because of the complexities involved in the photoelectric mechanism for solids which the Bohr theory has not yet encompassed, experimental facts of this sort do not bear vitally on the Bohr conceptions. On the other hand, experimental data on the photoelectric effect in vapours have a direct significance in the Bohr theory, inasmuch as in this instance the atoms are isolated and free to act the *rôle* to which the theory applies. Information of the latter sort is meagre. Steubing ‡ has described an experiment which seemed to show ionization in mercury vapour by light transmitted through fused quartz. Anderson § and Gilbreath ‖ have obtained ionization in potassium vapour which they attribute to a photoelectric effect in the vapour, but which probably resulted from a photoelectric effect from the electrodes. Kunz and Williams ¶ have observed

* A dissertation presented for the degree of Doctor of Philosophy at Yale University.

† Communicated by Professor W. F. G. Swann.

‡ *Phys. Zeit.* x. p. 787 (1909).

§ Phys. Rev. i. p. 233 (1913).

‖ Phys. Rev. x. p. 166 (1917).

¶ Phys. Rev. xv. p. 550 (1920); xxii. p. 456 (1923).

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a photoelectric effect in cæsium vapour having a threshold coincident with the limiting frequency of the principal series of the vapour, and Williamson * has indicated that the threshold for potassium vapour lies between 2800 Å. and 3100 Å., and has also shown that the efficiency of the light in producing the effect increases rapidly with the frequency. The present paper is an account of an experimental investigation of a more quantitative nature of the photoelectric effect in potassium vapour.

Experimental Arrangements.

The investigation of the photoelectric effect in vapours involves fundamental experimental difficulties, some of which are augmented when potassium vapour is used. It is well known that potassium is exceedingly active photoelectrically and thermionically, and the difficulties in differentiating a true photoelectric effect in the vapour from thermionic currents and photoelectric currents from the electrodes and other portions of the chamber are obvious. Various experimental methods were tried, culminating in the adoption of a method similar to that which Williamson used in his investigation. It became clear that the electrodes involved in measuring the ionization had to be kept at a temperature low relative to the temperature of the vapour requisite to produce sufficient vapour density. To meet this condition a jet of potassium was caused to traverse a chamber and condense on a liquid-air-cooled surface. The ions produced by light passing through the jet of vapour were collected by an arrangement of electrodes in a cool portion of the chamber. A collimating and diaphragming system caused the light to traverse the jet without impinging on metal parts of the chamber, thereby reducing to a minimum spurious photoelectric effects. In this way thermionic effects were reduced to a negligible order of magnitude, and restricted photoelectric effects from the electrodes and other portions of the chamber practically to effects arising from light scattered by the vapour.

The experiment was primarily a determination of the magnitude of the photoelectric ionization in the vapour per unit intensity of light as a function of the frequency. Hence a source of monochromatic light sufficiently intense to produce measurable photoelectric effects, and a means of measuring the light of intensity simultaneously with the observation of the effect in the vapour, were essentials.

* Phys. Rev. xxi. p. 107 (1923).

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Preliminary experiments showed that quartz-mercury lamps were totally inadequate sources of illumination, and that light from a Pfund iron arc resolved into bands of from forty to eighty ångströms produced measurable ionization in the potassium vapour. It perhaps is of interest to note in this connexion that the photoelectric effects in the vapour produced by these relatively small bands of wave-lengths from the iron arc were as large as the effects obtained from the whole spectrum of a quartz mercury lamp. The intensity of the light was measured by a potassium photoelectric cell which in turn was calibrated by a thermopile and galvanometer.

Figs. 1 and 1 *b* show diagrammatically the arrangement of the apparatus. Distilled potassium K in the reservoir R

Fig. 1.

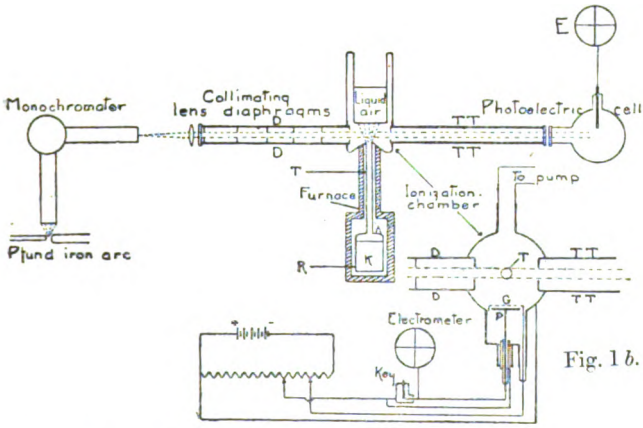

Fig. 1 *b*.

was heated by a furnace, causing a jet of vapour to issue up through a tube T (20 cm. in length) into the ionization chamber and on to a liquid-air-cooled surface, as the dotted lines indicate. Of course the jet was in no sense of the word unidirectional, and a good portion of the vapour entering the chamber condensed on portions of the chamber other than the liquid-air flask. Dotted lines also indicate the course of the light which, originating in the Pfund arc, passed into a monochromator. The band of wave-lengths from the monochromator after collimation by a quartz lens passed through a quartz window into a tube D (50 cm. long) containing a series of diaphragms. From the diaphragms the light passed into the ionization chamber, traversing the stream of vapour and out through a diaphragm into a

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second tube TT, and finally out through a quartz window into an adjacent photoelectric cell. The last diaphragm of the series in tube D was larger than the others, so that sensibly none of the light in the beam impinged on it. This last diaphragm cut off from the ionization chamber diffusely scattered light in the tube D, which was due to reflexions of the beam from the edges of the adjacent diaphragms. The single diaphragm in tube TT also was larger than the cross-section of the light beam, so that no portion of the bean suffered reflexion back into the chamber before entering the tube. The diagram does not properly indicate the orientation of the quartz window at the end of TT, as it was mounted so that the normals of its surfaces were at an angle with the direction of the beam of light passing through. This caused reflected light to strike the walls of the tube and to experience many reflexions before re-entering the ionization chamber. Both the interior of the tubes and the diaphragms of D and T were black. This optical system accomplished the purpose of preventing light from the monochromator striking any portion of the chamber appreciably (visible light passed through the chamber in this manner produced no discernible illumination therein). As has been mentioned before, this rather elaborate system of collimation of the beam was necessary, as without it stray light falling on the electrodes produced large spurious effects. This fact revealed itself early in the preliminary experiments.

The photoelectric cell placed at the exit end of TT to measure the intensity of the light passing through the vapour was of the Hughes * type, consisting of a flask coated on the interior with pure potassium metal. Light entering the cell through a quartz window experienced many reflexions on the potassium surface, thereby producing relatively large photoelectric currents in the cell. The sensitivity of the cell could have been further increased in the well-known manner by the introduction of suitable gases, but it was desired to have the potassium surfaces as free from contamination as possible, in order that existing data on the photoelectric selectivity of potassium could be made use of in a qualitative way. The diagram indicates an electrometer E attached to the cell. The electrometer measured the currents in some instances by the simple rate of deflexion method, and at other times the electrometer measured the fall in potential which the photo currents

* Hughes, Phil. Mag. xxv. p. 679 (1913).

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produced in passing through india ink resistance of the order of magnitude of 10^{10} ohms. The india ink resistance method ultimately was used entirely, as it was found in every respect more desirable.

The furnace surrounding the reservoir and jet tube was of brass tubing wound with resistance coils embedded in alundum cement, and was insulated thermally by asbestos. It possessed sufficient "heat inertia" to ensure that temperature changes were slow.

Fig. 1 *b* is a horizontal section of the ionization chamber depicting the electrode arrangement. The circle in the centre D represents the jet, and the dotted lines indicate the course of the light in its passage through the chamber across the vapour. The electrodes G, P are in a cool portion of the chamber at the side of the vapour jet. Because of the abundance of stray electrons of thermionic origin always present, the positive ions formed in the jet by the light were measured. An accelerating potential (relative to the positive ions) between the walls of the chamber and a grid G drew the positive ions to the grid, where a good share passed through and after traversing a smaller retarding field impinged on a plate P. An attached electrometer system deflected this positive ion current on to the plate. As was the case for the photoelectric cell currents, in this instance also both the rate of deflexion method and the high resistance method were used, culminating in the adoption in the final experiments of the latter. For simplicity the diagram indicates the arrangement for measuring the positive ions by the rate of deflexion of the electrometer. The modification involved in using the resistance method is perfectly obvious. For the rate of deflexion method an electrometer sensitivity was used of 800 mm. per volt, while for the resistance method the Dolezalek electrometer had a sensitivity of 6000 mm. per volt at a scale distance of 1·6 m. and was critically damped. The resistances used were of the order of 5×10^{10} ohms, and were made of fine ruled lines of india ink on paper hermetically sealed in glass tubes.

Constructional details of the apparatus hardly merit further description. Suffice to say that the ionization chamber and the tubes D and TT with diaphragms were of brass, and the jet and reservoir and the liquid-air flask were of pyrex glass and were attached to the brass ionization chamber by wax joints. Because of the high temperature of the jet an air blast played over the wax joint, keeping it properly cooled.

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Mercury diffusion pumps in conjunction with a liquid-air trap and McLeod gauge comprised the vacuum system.

Experimental Procedure.

The ionization chamber (and appending parts) was exhausted by the pump system to pressures which registered on a McLeod gauge less than 10^{-5} mm. of mercury. This vacuum was maintained during the course of a day, during which time potassium metal was distilled into the boiler. From the time of distillation of the metal to the completion of an experimental run the pumps were kept on the apparatus, thereby continually removing gases evolved from the metal and other portions of the chamber. After the completion of the distillation of the potassium into the apparatus immediately the iron arc and monochromator were adjusted so that light of maximum intensity passed through the chamber. Clearly this was obtained by an adjustment for a maximum current from the photocell. The furnaces were then turned on and brought to a fairly constant temperature in the neighbourhood of 300° C., and with suitable potentials on the electrodes the apparatus was ready for the observation of the photoelectric effects.

Preliminary experiments had shown that light of wave-length greater than 3000 ångströms apparently produced no appreciable photoelectric effects in the vapour, so that wave-lengths only of this order or shorter were used in the final experiments. It was found that a fairly intense band of wave-lengths emerged from the monochromator set at 2560 angströms (with slit-widths of 1 mm.), which produced a very readily measurable effect in the ionization chamber. The monochromator was set at this adjustment at the beginning of a run, and when conditions became steady, that is to say when both photo currents were observed to be quite constant, their magnitudes were taken down, and immediately the monochromator was adjusted to a new wave-length setting and the new values for the photo currents were noted. Next an observation with the former setting was made as a check on any change in conditions between observations. Clearly this procedure of taking observations in groups of three wherein the first and third were for the same wave-length permitted a close check on the variation of such things as the vapour density in the jet. This method of observation was extended over the whole range of useful wave-lengths, that is to say from 2200 ångströms on up. Inasmuch as the vapour rapidly distilled

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out of the boiler, it was necessary to work as quickly as possible. Observations were taken at the rate of about one per minute, a greater speed being prohibited by the natural period and damping of the deflexions of the electrometer needles. However, inasmuch as a run lasted over two hours, it was possible to get a fair number of readings over the whole range of investigation. Perhaps it should be mentioned in this connexion that with advancing time the level of the molten potassium in the reservoir lowered, and in order to maintain the same vapour density in the jet the temperature of the furnaces was gradually raised to compensate the effect of the change in position. The approach of the complete disappearance of the potassium from the reservoir evidenced itself very markedly by a lowering of the vapour-pressure in the jet and consequent ultimate disappearance of the photoelectric currents in the ionization chamber.

As has been mentioned above, the photoelectric currents were measured either by the rate of deflexion of the electrometer needles, that is by the deflexion during a definite period of time, or by the fall in potential produced by the currents flowing through high resistances of india ink. The latter case involves simply noting the deflexion of the electrometer when things are in equilibrium, while the rate of deflexion method is liable to error unless certain considerations are recognized. If the observed deflexions are to be proportional to the currents, Professor Swann * has pointed out that the deflexions must be taken over periods of time which are multiples of the natural period of oscillation of the electrometer needle. A subsidiary requirement also is that the period of observation must not extend from the time of opening the electrometer key, but from a short time later—of the order of one or two seconds. With this in mind, the two methods gave consistent values for the observed currents.

Results.

This experimental investigation was begun at the University of Chicago during the last academic year, and has been continued during the present year at Yale University. In view of the differences in the experimental apparatus at both places, it is desirable to present the results separately. As will be indicated below, the results of last year's work seemingly are at variance with what would be expected from

* Swann, Phil. Mag. xxiv. p. 445 (1912).

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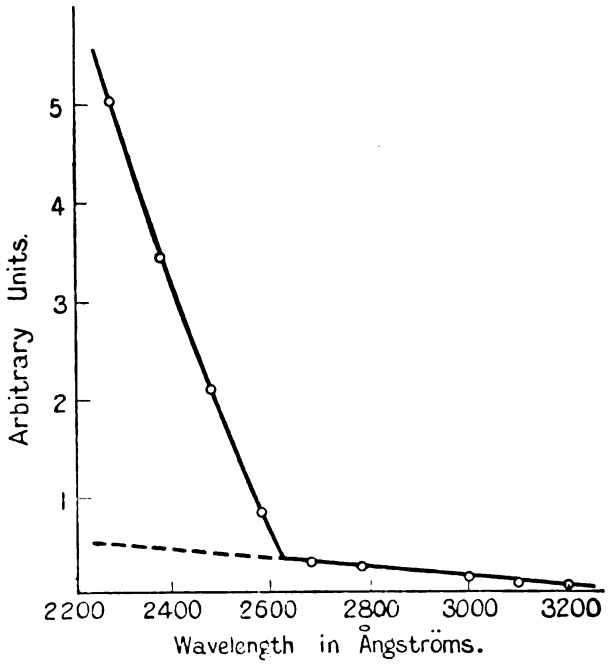
the Bohr standpoint, and the results of the present year form a rather significant check on the preceding year's work.

Fig. 2.—"Chicago Data."



Ordinates are ratios (arbitrary constant):—

$$\frac{\text{Photoelectric effect in potassium vapour.}}{\text{Photoelectric effect in potassium photocell.}}$$

Abscissæ are:—

Mean wave-length of band of wave-lengths producing photoelectric effects simultaneously in vapour and in photocell.

Both photoelectric currents measured by rate of deflexion method with electrodes at following potentials:—

Walls of ionization chamber	0·0 volts.
Grid	−12·0 ,,
Plate	−10·8 ,,

The curve of fig. 2 embodies the results obtained last year at Chicago. This typical curve is for a single experimental run—that is to say, it represents the data obtained during the time that a single reservoir full of potassium distilled into the ionization chamber. The points of the curve are the averages of the observations during the run corrected

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for changes in the density of the vapour-stream, as indicated in a paragraph of the experimental procedure. The ordinates are the ratios (times an arbitrary constant) of the photoelectric currents from the vapour to the photo currents from the photocell, produced by bands of wave-lengths emerging from the monochromator when adjusted at a wave-length setting given by the abscissæ. It is clear that if the photocell were equally sensitive to all wave-lengths, and the light emerging from the monochromator were monochromatic, the curve would represent the variation of the photoelectric effect in the vapour per unit light intensity with the frequency. Neither of these conditions subsisted in the experiment, so that the curve representing the variation per unit intensity with the frequency has a somewhat different form.

A Hilger monochromatic illuminator was used at Chicago, and the data of the above curve were obtained with slit-widths of 1·2 mm. A spectroscopic examination of the quality of the light emerging from the monochromator revealed that roughly 90 per cent. of the light was contained in bands of from fifty to a hundred ångströms (depending on the wave-length setting), which were symmetrical with respect to the wave-length for which the monochromator was adjusted. The remaining portion of the light was distributed throughout the spectral range, and of especial significance was the fact that there was always transmitted some light of much shorter wave-lengths. With this information it is possible to get at the significance of the curves.

The curve is represented quite closely by two intersecting straight lines, and is linear over intervals about the experimentally given points through which the curve is contructed. This point of intersection strikingly suggests itself as the photoelectric threshold for the vapour—that is, the abscissa of this point is the longest wave-length able to produce a photoelectric effect in the vapour. The photoelectric effects observed for wave-lengths greater than this threshold value represented by the portion of the curve to the right of the intersection are attributed to stray light of shorter wave-lengths transmitted by the monochromator, and to a photoelectric effect from the electrodes due to a small amount of scattered light.

Now let us consider the experimental points making up the portion of the curve to the left of the threshold. The photoelectric effects here arise from both stray effective wave-lengths and the bands of wave-lengths symmetrically placed about the values given by the abscissæ. Because of

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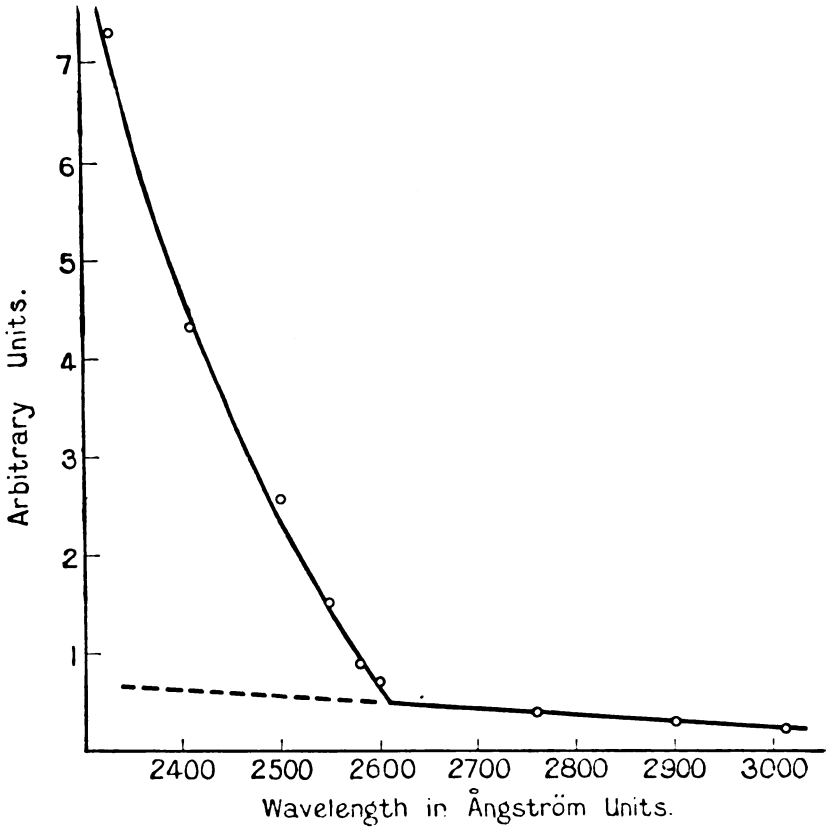
the linearity of the curve over these bands, it is clear that the assigned abscissæ are approximately the effective mean values for the wave-lengths of the bands, and allowing for the stray light, this portion of the curve represents the variation of the ratio of the photoelectric effect in the vapour to the effect in the photocell with the wave-length.

Fig. 3.—"Yale Data."



Ordinates and abscissæ same as Fig. 2.

Photoelectric currents measured by high-resistance method with electrodes at the following potentials.

Walls of ionization chamber	0·0 volts.
Grid	−22·0 ,,
Plate	−19·8 ,,

The amount of spurious effect in this region has not been determined, but probably is not far from that obtained by

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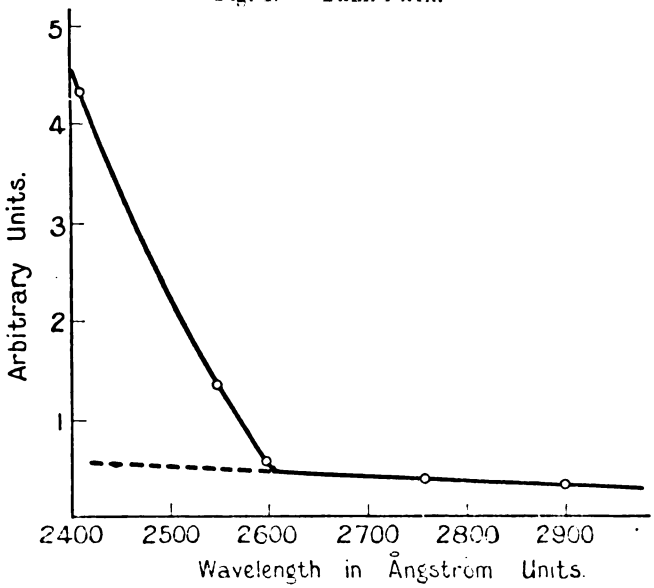
extrapolating from the portion to the right of the threshold, as indicated by the dotted lines.

Significant evidence of the trustworthiness of these results is given by the more recent experiments at Yale. The curves of figs. 3 and 4 are representative of the later results, and are seen to be of the same form as previously obtained at Chicago (fig. 2). There were two changes in the Yale apparatus of importance—namely, the monochromator and the photoelectric cell. A Gaertner instrument was used with

Fig. 4.—"Yale Data."



Ordinates and abscissæ same as for fig. 3.

Currents measured by high-resistance method with electrodes at following potentials:—

Walls of ionization chamber	0·0 volts.
Grid	−11·0 ,,
Plate	− 9·9 ,,

slit-widths of 1 mm. (giving wave-length bands of forty to eighty ångströms) and a new photocell was built similar to the one used at Chicago. In view of these changes, it is interesting to note the agreement in the threshold values obtained, an agreement perhaps more complete than should be expected. Of interest also is the similarity of the curves to the right of the threshold, which suggests that either the two monochromators are quite equally defective in their

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function of producing monochromatic light, or that in all instances the amount of scattered light was about the same. This latter possibility suggests that the vapour was responsible for the scattering. The form of the results embodied in the above curves is a function of the selectivity of the photoelectric cell. This accounts for the more pronounced curvature of the Yale curves (figs. 3 and 4). Finally, the data indicate that the observed photoelectric effects in the vapour are practically independent of both the potentials on the electrodes in the ionization chamber and the condition of the vacuum. In all cases the photoelectric effects observed have been of the form exhibited above, although a range of potentials from eight to twenty-two volts has been used, and the vacuum, as indicated on a McLeod gauge, has ranged from 10^{-3} mm. to 10^{-5} mm.

Because of the difficulties in measuring light intensities in the ultra-violet, the calibration of the photocell lacked precision and was extended only to 2580 ångströms. It was found that the selectivity of the cell was qualitatively similar to that of new potassium metal surfaces as found by Souder *. On the basis of this calibration, the probable variation of the photoelectric effect in the vapour per unit intensity of light as a function of the wave-length is given by the curve of fig. 5. Although a slight curvature is exhibited—suggesting a maximum—it is entirely possible that more reliable intensity measurements will show that this is a linear relation. It is hoped that this point will be settled in the near future. For the present, it can be asserted that only light of wave-length shorter than 2610 Angström units is able to produce a photoelectric effect in a stream of potassium vapour, and that the magnitude of the effect per unit light intensity is greater for shorter wave-lengths.

Williamson † has interpreted his results as indicating the photoelectric threshold at the Bohr theoretical value, namely 2856 ångströms. However, it is interesting to note that his published data are well in accord with the value herein given. It is interesting further to observe that the present results confirm his conclusion that light of shorter wave-lengths is more efficient in producing the photoelectric effect in the vapour jet, and that the general effects observed were independent of the electrode potentials,

* Phys. Rev. viii. p. 310 (1916).
† Phys. Rev. xxi. p. 107 (1923).

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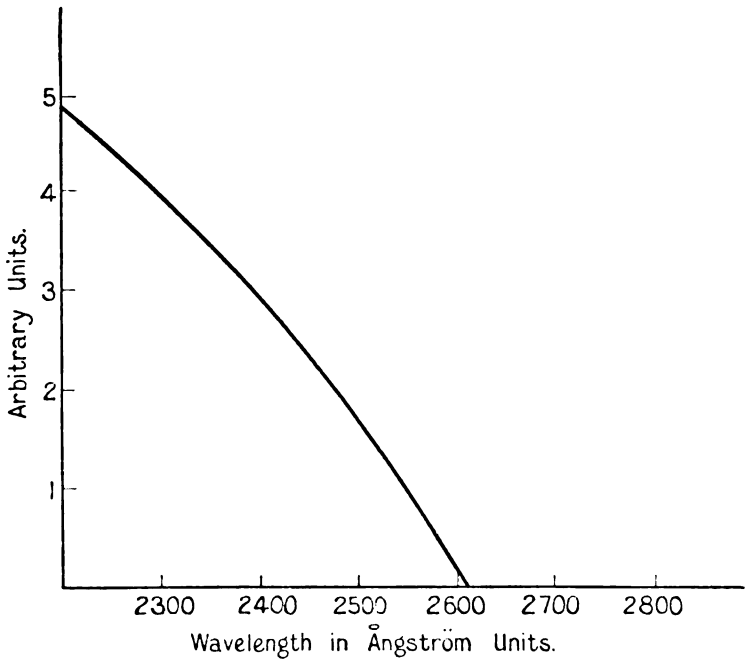
including potentials below the ionization potential of the vapour.

Discussion.

Researches on the absorption of light in alkali vapours reveal that wave-lengths of the principal series are absorbed as well as wave-lengths shorter than the series limit. The Bohr theory attributes the former phenomenon to the

Fig. 5.

Photoelectric effects in stream of potassium vapour per unit intensity of light.



Ordinates are photoelectric currents produced in vapour produced by light of wave-length given by abscissæ.

Photoelectric threshold at 2610 ångströms.

energy given up by the light in removing electrons from the 1*s* to the various *p* orbits, and the latter to a photoelectric effect. Light-quanta of greater frequency than the series limit have more than enough energy to eject an electron from the atom, and the surplus is used in giving the electron a velocity after ejection.

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Corresponding phenomena occur in the X-ray region. There an absorption is observed which decreases approximately as the cube of the wave-length from the K, L, and M limits. In this instance also the absorbed energy goes into the jumps of the electrons from various orbits and their velocity upon complete removal from the atom. The velocities of these X-ray photoelectrons have been measured and found to agree with this view, and in general all the experimental evidence supports this photoelectric origin of the absorption.

Continuous optical absorption of wave-lengths shorter than the series limit has been obtained by Wood * in sodium and by Holtsmark † in sodium and potassium, and more recently Harrison ‡ has published excellent photometric measurements of the variation of the absorption with the wave-length. Harrison's results indicate that the absorption decreases with the wave-length from the series limit in a manner similar to the decrease beyond the absorption limits in the X-ray region. By analogy with the X-ray photoelectric data this similarity suggests that this continuous absorption is due to a photoelectric effect in the vapour, in agreement with the Bohr theory. However, as has been pointed out, direct photoelectric evidence is meagre, and the present research was initiated with the hope of obtaining more definite data of this sort.

Williamson has discussed in detail the experimental evidence from which is concluded that the effects observed are photoelectric effects in the vapour. In the present instance it is sufficient to say that his evidence and conclusions have been confirmed. Now, clearly, the results obtained are completely in disaccord with expectations. Neither does the photoelectric threshold coincide with the limiting wave-length of the principal series, nor is the light of wave-length just less than the threshold the most effective in producing the photoelectric effect. If these results are truely representative of the photoelectric effect from potassium atoms in the vapour, we have here an apparent serious difficulty for the Bohr theory.

The most plausible explanation of the difficulty is that the vapour consists of aggregates of potassium atoms, most probably in a sort of diatomic molecular form. Then, if an energy of ·4 volt is assigned to that involved in dissociation,

* Astrophys. Journ. xxix. 97 (1909).
† *Phys. Zeit.* xx. p. 88 (1919).
‡ Phys. Rev. xxiv. p. 466 (1924).

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we have as the total energy required to ionize a molecule

$$\underset{\text{(Dissociation)}}{\cdot 4 \text{ volt}} + \underset{\text{(Ionization)}}{4\cdot 3 \text{ volts}} = 4\cdot 7 \text{ volts},$$

corresponding to the energy of a quantum of wave-length herein given as the threshold, viz. 2610 ångströms. That the vapour is in a molecular state receives support from other sources. Professor Wood * has observed channelled absorption bands in sodium vapour, and more recently H. D. Smith † has shown band absorption in potassium and other alkali vapours which strikingly suggests that a portion of the vapour is molecular. Clearly, if the number of such molecules is small relative to the number of atoms, the fact that the atomic photoelectric effect is not observed may be stated in another form, namely that the probability of a light-quantum ionizing a molecule is greater than that of its ionizing an atom.

Experiments are in progress designed to measure the initial velocities of the photoelectrons, and a method of positive-ray analysis is being developed to ascertain the nature of the photoelectric ions. Further theoretical speculation will be held in abeyance pending the outcome of this work.

Summary.

The photoelectric effect in a stream of potassium vapour has been observed, and it has been found that light of wave-length greater than 2610 ångströms produces no effect, and that the efficiency of the light in producing ionization increases as shorter wave-lengths are used. Because of the inconsistency with the Bohr theoretical interpretation of spectroscopic data on atomic potassium, the photoelectric effects observed are regarded as most probably due to a molecular state of the vapour.

The writer is very grateful to Professor W. F. G. Swann, who suggested the research, for his continued interest and many invaluable suggestions and criticisms throughout the course of the work, both at Chicago where the investigation was commenced and at Yale where it was completed.

Sloane Laboratory,
Yale University,
February 2, 1925.

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* Wood, 'Physical Optics,' 2nd edition.
† Smith, Proc. Roy. Soc. cvi. p. 400 (1924).

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XXXIV. *Note on Mr. Garner's Paper on the Critical Increment of Chemical Reactions.* By C. N. HINSHELWOOD, *Trinity College, Oxford* *.

THE occurrence of a bimolecular reaction in a gaseous system seems to depend upon collisions between molecules with high kinetic energy. Using an approximate form of the Maxwell distribution law this assumption leads to the following expression for the velocity constant k of the reaction

$$k = 2 \times \text{total number of collisions} \times e^{-Q/RT} \times P,$$

the factor $e^{-Q/RT}$ giving the fraction of the total number of collisions in which the energy is sufficiently great. The factor 2 is introduced because each fruitful collision involves the change of two molecules. P is a factor depending on the shape of the molecules (and possibly on internal "phase" factors) which expresses the probability that a collision between activated molecules results in the formation of the reaction products rather than in the separation of the two molecules in a chemically unchanged state.

Experimental evidence shows that P is of the order of magnitude unity—a result of considerable interest. Unless Q could be determined with a quite unattainable degree of precision, the nature of the above equation makes it impossible to ascertain the exact value of P. Nevertheless the knowledge that it is of the order of unity permits an absolute calculation of the logarithm of a velocity constant from the value of the heat of activation Q, in a manner well confirmed by experiment.

Q is obtained from the temperature-coefficient of k. The collision number is proportional to $\sqrt{T}$, whence

$$k = \text{constant } \sqrt{T}\, e^{-Q/RT};$$

thus $$d \log k/dT = \frac{1}{2T} + Q/RT^2.$$

In a recent communication to the Philosophical Magazine (1925, vol. xlix. p. 463) Mr. Garner points out that P cannot be exactly equal to unity. But it may be replied that in "irreversible" reactions there is no reason why P should not approach unity almost indefinitely. He also suggests that since P itself is an unknown function of temperature, the method of determining Q from the effect of temperature on the reaction velocity is unsound.

* Communicated by the Author.

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Unless I have misunderstood Mr. Garner's argument this criticism is not valid. Perhaps, at all events, it may be permissible to state the alternative view.

Temperature has no meaning applied to individual molecules. It defines the statistical distribution of energy among large numbers of molecules. Activated molecules are molecules with specified energies. Temperature determines how many of these exist and how many collisions take place between them. Whether a collision between two individual molecules with specified energies is "elastic" or "inelastic" in the chemical sense cannot depend upon the distribution of energy among other molecules which are not participating in the impact. Thus P would seem to be independent of temperature. "Activated" molecules have always the same "temperature" whatever the real statistical temperature of the gas may be, because they are *ex hypothesi* molecules of specified energy.

The use of the distribution law in the form $e^{-Q/RT}$ is of course not quite unobjectionable theoretically, but is justified by experiment within the limits of accuracy obtainable in the determination of Q.

Trinity College, Oxford.

XXXV. *Refraction and Electron Constraint in Ions and Molecules.* By CHARLES P. SMYTH, *Ph.D., Department of Chemistry, Princeton University* *.

IN the problems of molecular structure and chemical activity the outer electrons of the atomic shells are of prime importance and the constraints under which these electrons act may be decisive factors in determining the molecular behaviour. An approximately quantitative measurement of these constraints may be obtained from a consideration of the force necessary to displace the electrons from their positions of equilibrium or to alter or distort their orbits in the molecule. In the present discussion such an alteration or distortion will be treated as equivalent to a displacement of the effective position or position of equilibrium of the electron in the molecule. The force necessary to displace an electron may be calculated on the assumption that, when a small displacement occurs, the force tending to

* Communicated by the Author.

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restore the electron to its original position is proportional to the amount of the displacement, that is

$$\text{restoring force} = f \times \text{displacement},$$

in which f is a proportionality constant. When the displacement is unity, the restoring force is f, or f is the force which would be required to displace an electron one centimetre from its normal position in a molecule if the restoring force were always proportional to the displacement. Obviously, the relation cannot hold for a displacement of this magnitude, but, for very small displacements, such as those which cause refraction, it may be regarded as holding approximately. The constant f thus provides a measure of the resistance to the displacement of the electron.

In a previous paper* the writer has calculated f from relations which, for the purpose of the present paper, may best be expressed by the equation

$$\frac{m_\infty^2 - 1}{m_\infty^2 + 2} = \frac{4\pi N e^2}{3f},$$

in which m_∞ is the refractive index for light of infinite wave-length, N is the number of electrons in unit volume suffering displacement, and e is the electronic charge. This, by simple substitutions, may be converted to

$$f = \frac{4\pi N_0 n e^2}{3}\left(\frac{d}{w}\,\frac{m_\infty^2 + 2}{m_\infty^2 - 1}\right),$$

in which N_0 is Avogadro's number, $6{\cdot}061 \times 10^{23}$, n is the number of displaceable electrons per molecule, d is the density, and w is the molecular weight; or

$$f = \frac{4\pi N_0 n e^2}{3M_\infty},$$

where M_∞ is the molecular refraction for light of infinite wave-length. In the paper referred to f was calculated for a number of gases and, as great accuracy was neither required nor possible, refractive indices for light of visible wave-length were commonly used.

In a paper immediately subsequent to this, Born and Heisenberg † have used a somewhat similar expression to calculate the deformability, α, of an ion, α being defined by

* C. P. Smyth, Phil. Mag. xlvii. p. 530 (1924).

† M. Born and W. Heisenberg, *Z. Physik*, xxiii. p. 388 (1924).

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the relation $p = \alpha E$, in which p is the moment induced by a homogeneous electric field, E. The relation of α to f is given by the expression:

$$\alpha = \frac{ne^2}{f}.$$

By a combination of these calculations from refractive indices with deductions from values for the terms of spectral series, Born and Heisenberg obtained the deformability of the ions of a large number of elements. It is evident that α is proportional and f inversely proportional to the molecular or ionic refraction, and Fajans and Joos * have used the refraction as a direct measure of the deformability of the electron shells. These investigators have calculated the molecular refractions for the D-line, obtaining results in fair agreement with those for the D-line obtained by Wasastjerna for the rare gas atoms and a number of ions in an earlier investigation † and with those calculated from the values of α given by Born and Heisenberg. The refractions calculated for infinite wave-length should provide a sounder theoretical basis for the treatment of the electron constraints, but as the difference in wave-length causes but a small part of the differences between the results of Fajans and Joos and those of Born and Heisenberg, other factors contributing more largely, and as in other cases to be considered the data are often inadequate for extrapolation to infinite wave-length, it seems best in the present paper to use the values for the D-line. Although the differences between the different sets of data are, as a rule, too small to affect the conclusions to be drawn, the following tabulation of the results lays most weight upon the values of Fajans and Joos because they are obtained for the D-line and because these investigators took into account certain complications not provided for by Wasastjerna. The refractions are those which the atoms or ions should have when so isolated as to be practically unaffected by the fields of neighbouring atoms or ions. Table I. gives below the symbol of the atom or ion its refraction for the D-line, and below that the value of f for an electron in the outer shell.

The investigators whose results are shown in Table I. have noted the increase in refraction on passing downward in a column in approximate conformity to the relation observed

* K. Fajans and G. Joos, *Z. Physik*, xxiii. p. 1 (1924).

† J. A. Wasastjerna, *Z. physik. Chem.* ci. p. 193 (1922); *Soc. Scient. Fennica, Commentationes Physico-Math.* i. p. 37 (1923).

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by Cuthbertson *, and the decrease in passing along a period from left to right showing increase in constraint with increasing nuclear charge. In the paper already referred to, the writer noted the uniform decrease in f on going from neon to xenon through the family of the rare gases, and from fluorine to iodine in the diatomic molecules of the halogens. In calculating f it was assumed that all the electrons in the outer layer of the atom or those whose orbits extended farthest out from the nucleus were capable

TABLE I.

Ionic Refractions and Values of f.

			He	Li^+		Be^{++}		B^{+++}		C^{++++}
R_D			·50	·20		·09		·05		·03
$f\times10^{-6}$			2·32	5·8		12·9		23·2		38·6
	O^{--}	F^-	Ne	Na^+		Mg^{++}		Al^{+++}		Si^{++++}
R_D	7	2·5	1·00	·50		·29		·17		·1
$f\times10^{-6}$	·66	1·85	4·63	9·27		16·0		27·3		46·3
	S^-	Cl^-	A	K^+	Ca^{++}		Sc^{+++}		Ti^{++++}	
R_D	15	8·7	4·20	2·23	1·35	Zn^{++} †	·97		·69	
$f\times10^{-6}$	·31	·53	1·10	2·08	3·43	·29	4·78		6·72	
	Se^{--}	Br^-	Kr	Rb^+	Sr^{++}	16·0	Y^{+++}		Zr^{++++}	
R_D	16·3	12·2	6·37	3·6	2·25	Cd^{++}	2·6		2·03	
$f\times10^{-6}$	·28	·38	·73	1·29	2·06	2·44	1·78		2·28	
	Te^{--}	I^-	X	Cs^+	Ba^{++}	1·90	La^{+++}		Ce^{++++}	
R_D	24·4	18·5	10·42	6·3	4·3	Hg^{++}	4·0		3·05	
$f\times10^{-6}$	·19	·25	·445	·74	1·08	5·05	1·16		1·52	
						·92				

† The enclosed column is displaced one line down to show that its figures should not be directly related to those in the adjacent columns.

of suffering displacement and thus contributing to the refraction, the others being too rigidly bound to have an appreciable effect upon the refraction. In the neon and argon atoms the number of displaceable electrons should be eight, and the assumption of eight in krypton and xenon led to the uniformly decreasing values of f already mentioned as compared with the fact that the assumption of eighteen as indicated by the original theory of Langmuir caused a sharp increase in going from argon to krypton followed by a decrease in the value for xenon.

In calculating the values of f in Table I. eight displaceable

* C. Cuthbertson, Trans. Roy. Soc. London, cciv. p. 323 (1905); 'Science Progress,' x. p. 1 (1908). C. Cuthbertson and E. B. R. Prideaux, Trans. Roy. Soc. London, ccv. p. 319 (1905). C. Cuthbertson and E. P. Metcalfe, Trans. Roy. Soc. London, ccvii. p. 135 (1907). S. Smiles, 'The Relation between Chemical Constitution and some Physical Properties,' 1910, p. 245.

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electrons are assumed for all but the elements in the first line, which contain but two electrons. The values of f in the first period are lower than those in the second, possibly because of the absence of screening effect in the structures of the first period. No distinction can be made between the electrons of the same total but different azimuthal quantum numbers indicated by the Bohr theory, so that f may be but an average value in the case of most of the ions.

Since Fajans and Joos and Born and Heisenberg, in their papers which came out shortly after the writer's preliminary discussion of the quantity f, have given a detailed treatment of the refractions and deformabilities of the atoms and ions in Table I., discussion of the corresponding values of f appears unnecessary. However, some interesting relations appear when f can be calculated for electrons which form valence bonds between molecules. In the preliminary treatment of the subject f was calculated for the electrons in a number of simple molecules, the results thus obtained being averages of the values for electrons in different parts of the molecules. The work of Fajans and Joos and Born and Heisenberg has shown that the constraint upon an electron in an ion is increased by the proximity of other ions or molecules, particularly if actual combination occurs. This may be illustrated by the comparison in Table II. of the values

TABLE II.*

Molecular Refractions and Values of f for the Halogen and Hydrogen Halides.

	R_D.			$f \times 10^{-6}$.		
X	X^-	HX	X_2	X^-	HX	X_2
F.....	2·5	(1·9)	2·91	1·85	(2·44)	2·79
Cl	8·7	6·68	11·67	·53	·69	·69
Br	12·2	9·14	17·43	·38	·51	·47
I	18·5	13·75	31·97	·25	·34	·25

of R_D and f for the halogen ions with those for the hydrogen halides and the diatomic halogen molecules, the number of displaceable electrons in the latter being taken as fourteen.

If it could be assumed that the attachment of a hydrogen nucleus to a halogen ion to form a hydrogen halide molecule

* The values for the ions are taken from Table I., the refraction of hydrogen fluoride is a value estimated by Fajans and Joos, and the other values are calculated from data contained in Landolt-Börnstein, 5th edition.

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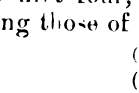
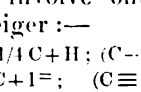
affected only the two electrons which are supposed to form the valence bond, the contribution to the molecular refraction of the other six electrons in the outer layer would be three-fourths of the ionic refraction, and that of the two binding electrons would be the difference between this and the molecular refraction. In the case of the hydrogen halides, this difference is practically zero, which might seem to indicate that the binding electrons are under such rigid constraints as to be incapable of being appreciably displaced, but in some cases where the bonds must be more rigid the contribution to the refraction of the binding electrons appears to be a negative quantity when calculated in this way, which shows that the electrons other than those forming the bond suffer a loss of mobility, although they are probably less rigidly constrained than the binding electrons. Presumably, all the outer electrons contribute to the molecular refraction in greater or less degree according to their positions in the molecule. The average values of f show that the bond in the fluorine molecule produces a greater decrease in electron mobility than that in the hydrogen fluoride molecule, but, with increasing atomic diameter, the effect of the bond in the halogen molecule diminishes until the electrons in the I_2 molecule are hardly more constrained than those in the I^- ion, which is consistent with the increasing ease of dissociation of the molecules with increasing atomic weight. On the other hand, the effect of the bond in the hydrogen halide molecule increases slightly with increasing atomic weight, a phenomenon which will be discussed presently.

Instead of calculating the average value of f for a number of differently situated electrons in a molecule, it is simpler to consider the contribution of this group of electrons to the molecular refraction. Contributions of this character may be calculated by means of the simple equations used by von Steiger * to calculate bond refractions from atomic refractions and other equations constructed on similar principles, of which the following are given as examples, the first four, which involve only carbon and hydrogen, being those of von Steiger :—

$$(C-H)=1/4\,C+H\,;\ (C-C)=1/2\,C\,;$$
$$(C=C)=C+1^{=}\,;\quad (C\equiv C)=3/2\,C+1^{\equiv}\,;$$


$:=1/4\,C+H+O'$; 
$:=1/2\,C+O<$; $C=O:=1/2\,C+O''$;

$C-\underset{\cdot\cdot}{X}:=1/4\,C+X$; $Si-\underset{\cdot\cdot}{Cl}:=1/4\,SiCl_4$; $S-\underset{\cdot\cdot}{F}:=1/6\,SF_6$.

* A. L. von Steiger, *Ber.* liv. p. 1381 (1921).

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In these equations, each line joining the atoms represents a bonding electron pair, and each dot a displaceable electron which does not enter into a bond. The refraction, in each case, is supposed to arise only from the electrons thus indicated. H, C, O′, O<, O″. X, $SiCl_4$, and SF_6 represent respectively the atomic or molecular refractions of hydrogen, carbon, hydroxyl oxygen, ethereal oxygen, carbonyl oxygen, a halogen, silicon tetrachloride, and sulphur hexafluoride, and $1^{=}$ and $1^{\equiv}$ are the refractions assigned to the double and the triple bond. The results calculated in this manner are given in Table IV., which shows each electron group with the value of its refraction to the right and a reference to the source of the data used to obtain this value. Whenever possible, use has been made of the average values for the atomic refractions given in well recognized tables, such as those of Eisenlohr *, and when data on individual substances have been employed the reliable results for all available substances have been averaged. As a check upon the results, the refractions of the electron groups may be used to calculate molecular refractions. The results in Table III., which gives some of these calculations for widely differing substances chosen as typical, show that the errors of this method are no greater than those due to experiment and to the minor differences of grouping which are so small as not yet to have been explained.

Table III.

Comparison of Calculated and Observed Molecular Refractions (D-line).

	Calculated.		Observed †.
$n-C_3H_7NH_2$ $i-C_3H_7NH_2$	$2(C-C)+7(C-H)+\begin{matrix}C\diagdown\\H-N:\\H\diagup\end{matrix}$	$=19{\cdot}48$	$\left\{\begin{matrix}19{\cdot}43\\19{\cdot}59\end{matrix}\right.$
C_2H_5OH	$(C-C)+5(C-H)+\begin{matrix}C\diagdown\\H\diagup\end{matrix}\ddot{O}:$	$=12{\cdot}96$	$12{\cdot}78$
$n-C_4H_9OH$ $(CH_3)_3COH$	$3(C-C)+9(C-H)+\begin{matrix}C\diagdown\\H\diagup\end{matrix}\ddot{O}:$	$=22{\cdot}20$	$\left\{\begin{matrix}22{\cdot}14\\22{\cdot}22\end{matrix}\right.$
$(C_2H_5)_2S$	$2(C-C)+10(C-H)+\begin{matrix}C\diagdown\\C\diagup\end{matrix}\ddot{S}:$	$=28{\cdot}65$	$28{\cdot}54$
CO_2	$2C=\ddot{O}:$	$=6{\cdot}84$	$6{\cdot}71$
CS_2	$2C=\ddot{S}:$	$=21{\cdot}22$	$21{\cdot}36$

† The observed molecular refractions are taken directly from Landolt-Börnstein, 5th edition, or calculated from the refractive indices there given.

* Landolt-Börnstein, 5th edition, p. 985.

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Table IV.

Refractions of Electron Groups.

H—H 2·08[1]				
C—H 1·705[1]			C—Zn 4·73[2]	C—Hg 6·91[3]
C—C 1·209[1]		C—Si 2·30[5]	C—Sn 4·02[4]	C—Pb 5·02[4]
C=C 4·15[1]				
C≡C 6·025[1]				
$\begin{matrix}H\\H\\H\end{matrix}\!\!>\!N$: 5·63[1]		$\begin{matrix}H\\H\\H\end{matrix}\!\!>\!P$: 11·9[6]		
$\begin{matrix}C\\H\\H\end{matrix}\!\!>\!N$: 5·13[1]				
$\begin{matrix}C\\C\\H\end{matrix}\!\!>\!N$: 4·81[1]				
$\begin{matrix}C\\C\\C\end{matrix}\!\!>\!N$: 4·65[1]		$\begin{matrix}C\\C\\C\end{matrix}\!\!>\!P$: 11·28[6]		
$\begin{matrix}H\\H\end{matrix}\!\!>\!\dot{O}$: 3·76[1]		$\begin{matrix}H\\H\end{matrix}\!\!>\!\dot{S}$: 9·57[1]		
$\begin{matrix}C\\H\end{matrix}\!\!>\!\dot{O}$: 3·23[1]	$\begin{matrix}Si\\H\end{matrix}\!\!>\!\dot{O}$: (4·1)[5]	$\begin{matrix}C\\H\end{matrix}\!\!>\!\dot{S}$: 9·40[7]	$\begin{matrix}C\\H\end{matrix}\!\!>\!\dot{Se}$: 12·34[8]	
$\begin{matrix}C\\C\end{matrix}\!\!>\!\dot{O}$: 2·85[1]	$\begin{matrix}Si\\C\end{matrix}\!\!>\!\dot{O}$: 3·24[5]	$\begin{matrix}C\\C\end{matrix}\!\!>\!\dot{S}$: 9·18[7]	$\begin{matrix}C\\C\end{matrix}\!\!>\!\dot{Se}$: 11·96[9]	$\begin{matrix}C\\C\end{matrix}\!\!>\!\dot{Te}$: 17·45[9]
$\begin{matrix}B\\C\end{matrix}\!\!>\!\dot{O}$: 3·39[6]				
$C=\dot{O}$: 3·42[1]		$C=\dot{S}$: 10·61[7]		
		$S-\ddot{F}$: 1·95[10]	$Se-\ddot{F}$: 2·23[10]	$Te-\ddot{F}$: 2·47[10]
	$B-\ddot{Cl}$: 6·99[10]		$B-\ddot{Br}$: 9·98[10]	
$C-\ddot{F}$: 1·60[11]		$C-\ddot{Cl}$: 6·57[1]	$C-\ddot{Br}$: 9·47[1]	$C-\ddot{I}$: 14·51[1]
		$Si-\ddot{Cl}$: 7·04[10, 1]	$Si-\ddot{Br}$: 10·21[10]	
		$Ti-\ddot{Cl}$: (9·32)[10, 1]		
		$Sn-\ddot{Cl}$: 8·63[10, 1]		

[1] Landolt-Börnstein, 5th edition, pp. 961–985.
[2] A. Ghira, *Gazz. chim. ital.* xxiv. p. 324 (1894).
[3] A. Ghira, *Atti Accad. Lincei*, (5) iii. A. p. 297 (1894).
[4] A. Ghira, *ibid.* p. 332 (1894).
[5] G. Abati, *Z. physik. Chem.* xxv. p. 353 (1898).
[6] F. Eisenlohr, *Spektrochemie Organischer Verbindungen*, pp. 69–72 (1912).
[7] T. S. Price and D. F. Twiss, J. Chem. Soc. ci. p. 1259 (1912).
[8] S. Smiles, 'The Relations between Chemical Constitution and Some Physical Properties.' p. 277 (1910).
[9] G. Pellini and A. Menin, *Gazz. chim. ital.* xxx., II. p. 465 (1900).
[10] K. Fajans and G. Joos, *op. cit.* p. 27.
[11] F. Swarts, *J. chim. phys.* xx. p. 30 (1923). The refractive effect of fluorine varies somewhat with the nature of the molecule containing it, but the value given for $C-\ddot{F}$: may be regarded as representative.

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The values in Table IV. show that the electrons binding two carbon atoms are more tightly held than those binding a carbon and a hydrogen atom, which, in turn, are more tightly held than the two electrons in the hydrogen molecule. If it is assumed, as indicated by the dashes connecting the atomic symbols in the table, that two electrons are shared in the single bond, four in the double, and six in the triple, the actual value of f for each electron in these bonds may be calculated, as well as the values for other bonds listed in Table V.

TABLE V.

Values of f for Bonding Electrons.

	$f \times 10^{-6}$
H—H	·56
C—H	·679
C—C	·958
C=C	·558
C≡C	·576
C—Si	·504

We do not know the distance of the hydrogen nucleus from the electrons in the C—H bond, but it is apparent that the hydrogen exerts less force on these electrons than does the carbon nucleus with its larger charge in the C—C bond. If it is assumed, as seems probable from the results of X-ray analysis, that the outer electrons in the atoms of the diamond have their effective positions located in pairs between the atoms, so that each atom may be treated as sharing a pair of electrons with each of four other atoms, the value of f for these electrons may be calculated from data on the refractive index and density of the diamond given in Landolt-Börnstein (5th edition). The value, $1{\cdot}10 \times 10^6$, is close to the figure, $\cdot 958 \times 10^6$, for the electrons in the C—C bond, but somewhat higher, as might be expected from the fact that the close packing in the diamond lattice probably gives opportunity for a given electron pair to be constrained by the force fields of atoms other than the two between which the pair lies. Although the silicon nucleus has a larger charge than the carbon, its greater distance from the electrons in the C—Si bond causes it to exert a smaller force upon them so that they are more loosely held than the electrons in the C—H bond.

The looser binding of the electrons in the double and triple bonds is in accord with the ease with which addition may occur at these bonds. The slightly greater constraint

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upon the electrons of the triple bond is in harmony with the fact that molecules containing this bond show, on the whole, less unsaturation than those containing the double bond, but the difference is too small to be significant. In the light of these relations, it is interesting to examine an hypothesis sometimes advanced to explain the structures of the molecules containing these bonds, namely, that the arrangement of the effective positions of the electrons is such that one pair occupies each apex of a regular tetrahedron, two tetrahedra sharing an apex in the case of a single bond, an edge in the case of a double bond, and a face in the case of a triple bond.

When two tetrahedra share an edge as assumed in the case of the double bond, the positive nuclei, supposed to lie at the centres of the tetrahedra, are brought closer together than in the case of the single bond and consequently repel each other more strongly. This increased repulsion tends to increase the distance between the nuclei, thereby increasing the distance of the nuclei from the bonding electrons at the two shared apices. The mutual repulsion of these two electron pairs acting along the shared edge tends to increase the length of this edge, thereby increasing the distance of the electron pairs from the positive nuclei, but this effect is opposed by the components along the edge of the attractive forces exerted by the positive nuclei. The net result of these effects would probably be an increase in the distance of the binding electrons from the positive nuclei and, as a consequence, the observed decrease in the constraints acting upon the electrons. In the case of the triple bond, the sharing of a face by two tetrahedra should bring the positive nuclei closer together than in the case of the double bond, the repulsion between the two nuclei being correspondingly greater. The repulsion between the electron pairs at the three shared apices should be greater because each pair would be acted upon by the resultant of the repulsive forces exerted by the other two pairs. Since the positive nuclei should be closer to the plane in which these forces act, the components in this plane of the attractive forces which they exert upon the electrons should afford greater opposition to the moving apart of the electron pairs than in the case of the double bond, but this increase in the attractive force should not be sufficient to balance the increase in the tendency of the electron pairs to move apart because of their mutual repulsion. One would, therefore, predict somewhat weaker constraints on the electrons in the triple bond than in the double, while the values of f show the

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electrons of the triple bond to be, if anything, a little more tightly held. The hypothesis of two tetrahedra sharing an edge in a double bond and a face in a triple bond gives a satisfactory explanation of the smaller electron constraint in these bonds as compared to that in the single bond, but fails to explain the almost equal constraints in the double and triple bonds, although the difference demanded by the hypothesis is not necessarily great and the failure may be due to the difficulty of taking proper account of all the variables. If this problem were considered from the ordinary point of view of atomic refractions, the greater refraction assigned to the triple bond would lead to the expectation of greater unsaturation and greater readiness to take part in addition reactions than in the case of the double bond.

The value of f, $\cdot 245 \times 10^6$, calculated for the electron pair of the C—Zn bond, shows the decrease of the electron constraint with increase in atomic diameter. The refraction, 4·73, calculated for this electron pair from the refractive indices of zinc methyl and zinc ethyl presumably contains a small contribution from the completed shell of electrons underlying the bonding pairs, as Table I. shows a value of ·29 for the refraction of the ion Zn^{++}, which must, however, be considerably decreased by the proximity of the other atoms in the zinc methyl and zinc ethyl molecules. The refraction, 6·91, calculated for the C—Hg bond from data on mercury dimethyl and mercury diethyl, contains a considerable contribution from the underlying shell of electrons in the mercury atom. If these electrons were unaffected by the other atoms in the molecule, this contribution would be one-half of the refraction of the Hg^{++} ion shown in Table I., or 2·53, but it is undoubtedly reduced by the fields of the other atoms in the molecule. If the value assigned to the C—Hg bond is doubled, the resulting figure, 13·82, is the refraction due to the two pairs of binding electrons together with that due to the underlying electron shell. This figure is close to the value, 13·94, calculated from data in Landolt-Börnstein and given by Fajans and Joos * for the atomic refraction of mercury vapour, the atoms of which contain two unshared valence electrons. The refractions of the C—Sn and C—Pb bonding pairs, which presumably contain contributions from the first underlying electron shells, show the usual decrease in electron constraint with increase in atomic size.

The rest of the refractions shown in the table are for

* *Op. cit.* p. 35.

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groups of eight electrons, one, two, or three pairs of which serve as bonds between atoms. The shell underlying this group of eight electrons can make no appreciable contribution to the refraction. The values for the $Ti-\ddot{\underset{\cdot\cdot}{Cl}}:$ and $Sn-\ddot{\underset{\cdot\cdot}{Cl}}:$ groups, the first of which loses somewhat in significance because of strong dispersion, presumably contain very small contributions from the underlying electron shells in the titanium and tin atoms, but contributions of this character should be negligible in the other groups.

In the values for the nitrogen electron group, calculated from data on ammonia and the amines, it is apparent that an attached carbon atom causes greater electron constraint than a hydrogen, the constraint increasing from the $\begin{matrix} H \diagdown \\ H-N: \\ H \diagup \end{matrix}$ to the $\begin{matrix} C \diagdown \\ C-N: \\ C \diagup \end{matrix}$ group. The difference in effect is less marked in the larger phosphorus electron group. Similarly, the carbon atom produces stronger constraint than the hydrogen when attached to an electron group of the oxygen family, but the difference in effect decreases as the volume of the group increases with accompanying decrease in the electron constraint. When a carbon atom attached to the group $\begin{matrix} C \diagdown \\ C \diagup \end{matrix}\dot{O}:$ is replaced by the larger atom of silicon, the electron constraint is decreased, and when the remaining carbon is replaced by a hydrogen to give the group $\begin{matrix} Si \diagdown \\ H \diagup \end{matrix}\dot{O}:$ a further decrease in the electron constraint is apparent, although the value of the refraction is somewhat uncertain because of the fact that it was obtained from measurements upon a solution of silicic acid. When a carbon atom is replaced by a boron atom with its smaller nuclear charge, a considerable decrease in the electron constraint is apparent, and the weaker forces exerted by the boron nucleus are evident again in the higher values for the refractions of the $B-\ddot{\underset{\cdot\cdot}{Cl}}:$ and $B-\ddot{\underset{\cdot\cdot}{Br}}:$ groups as compared with those for the $C-\ddot{\underset{\cdot\cdot}{Cl}}:$ and $C-\ddot{\underset{\cdot\cdot}{Br}}:$ groups. The relative effects of the carbon and hydrogen atoms in increasing the electron constraint is shown again by comparison of the refractions for the $C-\ddot{\underset{\cdot\cdot}{X}}:$ group with those for the $H-\ddot{\underset{\cdot\cdot}{X}}:$ group in Table II. A carbon atom

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attached to a fluorine group produces greater electron constraint than a hydrogen, the difference in the effects is smaller for the chlorine group, and, in the bromine and iodine groups, the attached carbon actually produces smaller constraint than a hydrogen. It is thus generally observed that, with increasing size of the electron group the difference between the effect of an attached hydrogen and that of an attached carbon becomes relatively smaller and may even reverse its sign. This may be explained by supposing that the carbon nucleus with its two electrons in the inner shell or K-level does not greatly alter its distance from the bonding electron pair as the volume of the electron group to which it is attached increases, but that the hydrogen nucleus approaches more closely to the bonding electron pair as the increasing distance of this pair from the nucleus of the electron group makes possible such an approach because of the decreasing repulsion of the two nuclei. Such an approach might actually extend to a penetration of the outer electron shell by the hydrogen nucleus, as suggested by certain investigators in the case of the hydrogen halides*. This approach would increase the force exerted by the hydrogen nucleus on the electrons as compared with that exerted by the carbon nucleus, thus causing the effect noted. It is apparent that the forces exerted upon the electrons in a group decrease as the volume of the group increases, and increase as the nuclear charge of an atom increases without increase in volume, as is the case in a horizontal period of the Periodic System.

In an attempt to determine the effect of a hydrogen nucleus attached to one atom in a molecule upon the electrons in the adjacent atoms of the molecule, the value for $C-\ddot{\underset{\cdot\cdot}{X}}:$ was calculated from the molecular refraction of a large number of halogen-substituted hydrocarbons, particular attention being paid to isomers. A number of cases were found in which a nearby hydrogen nucleus appeared to increase slightly the constraint upon a chlorine electron, and none in which it caused a decrease, but, as the differences noted were small, and as nothing definite could be drawn from the very limited data available for testing the other halogen compounds, the results were regarded as inconclusive.

The strong forces acting in the fluorine structure are

* H. Bell, Phil. Mag. xlvii. p. 549 (1924). M. Born and W. Heisenberg, *op. cit.*

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shown by the results of Swarts * for unsaturated fluorine substitution products. The replacement of a hydrogen by a fluorine atom in a saturated compound ordinarily causes a decrease in the molecular refraction of about 0·1, while a similar substitution at an unsaturated carbon causes a decrease of 0·2 to 0·6, presumably, because the fluorine structure tightens the constraint upon the loosely held electrons of the unsaturated bond.

Comparison of the refractions for the $C=\dot{O}:$ and $C=\dot{S}:$ groups with those for the $\begin{matrix} C \diagdown \\ C \diagup \end{matrix}\dot{O}:$ and $\begin{matrix} C \diagdown \\ C \diagup \end{matrix}\dot{S}:$ groups shows the smaller constraint of the electrons in the double bonds. The exaltation of the refraction in a conjugated system gives evidence of a loosening of the constraint upon the electrons in the neighbourhood of those in the double bonds, but the actual mechanism of this decrease in constraint cannot be clear until the phenomena of the double and triple bonds are better understood.

The refractions calculated for the electron groups in the hexafluorides of sulphur, selenium, and tellurium show an interesting progression. The value for $S-\ddot{\underset{\cdot\cdot}{F}}:$, 1·95, is larger than the value for $C-\ddot{\underset{\cdot\cdot}{F}}:$, 1·60, by no more than might be expected because of the larger size and hence lower electron constraint in the sulphur atom, while the value for $Te-\ddot{\underset{\cdot\cdot}{F}}:$ differs by a negligible amount from the refraction given for the fluoride ion in Table I. The group $Te-\ddot{\underset{\cdot\cdot}{F}}:$ would seem to be practically identical with the fluoride ion, although the stability and low boiling-point of tellurium hexafluoride are properties not ordinarily associated with substances whose molecules contain polar bonds. As the carbon-fluorine bond is one which would ordinarily be classed as non-polar, the electron groups under consideration apparently show a gradual transition from a polar to a non-polar type of linkage. One might regard the sulphur-fluorine bonds in sulphur hexafluoride as polar and consider that the refraction of the $S-\ddot{\underset{\cdot\cdot}{F}}:$ group is diminished by the attractive forces exerted by the sulphur nucleus, which does not differ materially from the situation existing if the bonds are non-polar. If the bonds are polar, we have fluoride ions

* F. Swarts, *op. cit.*

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arranging themselves more or less symmetrically about the central structure but somewhat deformed by the forces exerted by this structure. If the bonds are non-polar, we have an electron pair shared between each fluorine group and the central structure, but the location of these shared pairs may be identical with that which they would occupy in the case of the so-called polar linking, so that the distinction between the polar and the non-polar bond in molecules of this character is seen to be one merely of nomenclature.

A similar argument applies to the increase in refraction from $C-\ddot{\underset{\cdot\cdot}{Cl}}:$ through $Si-\ddot{\underset{\cdot\cdot}{Cl}}:$ to $Sn-\ddot{\underset{\cdot\cdot}{Cl}}:$, the value for which is only slightly lower than that given for the chloride ion in Table I.

Summary.

The forces opposing the displacement of the outer electrons in ions and molecules are calculated from the refractions. When the force cannot be calculated for an individual electron, the contribution to the refraction of a group of electrons is taken as an inverse measure of the average force acting upon these electrons. It is found that, where unsaturation exists, the constraint upon the electrons is low and that, in general, the forces exerted upon electrons shared between atoms, as well as those acting upon the unshared outer electrons of atoms or ions, decrease as the number of underlying electron shells increase and increase when the nuclear charge increases without increase in the number of underlying shells.

Princeton, New Jersey, U.S.A.
November 1, 1924.

XXXVI. *Multiplet Structure. By* Arthur Bramley, *Ph.D., Fellow in Physics, Princeton University* *.

THE equations of motion of an electron, describing a path about a central charge, without radiation of energy, can be written in the form

$$\frac{d^2x^i}{ds^2} + \Gamma^i_{\alpha\beta}\frac{dx^\alpha}{ds}\frac{dx^\beta}{ds} = 0,$$

where the Γ's are sets of functions depending on the position of the charge and electron.

* Communicated by the Author.

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The general quadratic solution of the above set of equations is of the form

$$e^{\int \phi_\alpha dx^\alpha}\left[g_{ij}\frac{dx^i}{ds}\frac{dx^j}{ds}\right] = \text{const.},$$

where the ϕ_α is a vector which becomes in the above case the momentum of the moving charge in the x^α direction, and g_{ij} is a tensor of the second order *.

If the solution is periodic, then

$$\int p_\alpha\, dx^\alpha = n\kappa,$$
$$\kappa = \text{const.},$$
$$p_\alpha = \text{momentum in the } x^\alpha \text{ direction.}$$

The relative invariant integral

$$\int p_\alpha\, dx^\alpha$$

is equal to the absolute invariant integral

$$\iint \delta p_\alpha\, \delta x^\alpha,$$

where each double integral is taken over the projection of the section of the tube of paths on the corresponding $p_\alpha q_\alpha$ plane. The integral

$$\iint \delta p_\alpha\, \delta x^\alpha = n\kappa$$

can be reduced to a system of one degree of freedom invariantly so that we get

$$\int p_\alpha\, dx^\alpha = n\kappa,$$

α not summed.

This gives the familiar quantum integrals for the three spatial components, but in addition it leads to the quantization of the time momentum

$$\int p_4\, dt = n\kappa,$$

which is a necessary consequence of the idea that the spatial and time directions have equal significance.

The above argument has been given for the three spatial components by E. P. Adams ('Quantum Theory,' p. 38). The considerations outlined above lead to the conclusion that only tubes of paths can exist in the four-dimensional manifold which are multiples of unit tubes.

The fundamental quadratic form associated with the motion of an electron about a central charge E is

* Eisenhart, Trans. of A. M. S., July 1924.

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$$H = 2m\left[\left(\frac{dr}{ds}\right)^2 + r^2\left(\frac{d\theta}{ds}\right)^2 + r^2\sin^2\theta\left(\frac{d\phi}{ds}\right)^2\right] - \left(1-\frac{eE}{r}\right)\left(\frac{dt}{ds}\right)^2,$$

where

H = energy of the electron,
m = mass of the electron,
e = charge on the electron ;

or

$$H\left[1+\frac{1}{H}\left(\frac{dt}{ds}\right)^2\right] = 2m\left[\left(\frac{dr}{ds}\right)^2 + r^2\left(\frac{d\theta}{ds}\right)^2 + r^2\sin^2\theta\left(\frac{d\phi}{ds}\right)^2\right] + \frac{eE}{r}\left(\frac{dt}{ds}\right)^2.$$

If we consider the spatial quantum integral, *e. g.*

$$\int g_{11}\left(\frac{dr}{ds}\right)dr = \kappa n,$$

then we have

$$\int 2m\left(\frac{dt}{ds}\right)\left(\frac{dr}{dt}\right)dr = \kappa n,$$

but

$$m\left(\frac{dt}{ds}\right) = m_0,$$

the invariant mass of the electron, and our invariant integral becomes

$$2m_0\int\left(\frac{dr}{dt}\right)dr = \kappa n,$$

the familiar law where

$$\kappa = h = \text{Planck's constant.}$$

Considering next the time component, we have

$$\int g_{44}\frac{dt}{ds}dt = hn,$$

or

$$\int\left(1-\frac{eE}{r}\right)\left(\frac{dt}{ds}\right)^2 ds = hn.$$

But from the integral of the equation of motion,

$$\frac{d^2t}{ds^2} + \frac{d}{dr}(\log g_{44})\frac{dr}{ds}\frac{dt}{ds} = 0,$$

we have

$$g_{44}\left(\frac{dt}{ds}\right) = \text{const.},$$

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which is analogous to the equation of areas,

$$g_{22}\left(\frac{d\theta}{ds}\right) = \text{const.}^*$$

Hence our time invariant integral becomes

$$\int\left(g_{44}\frac{dt}{ds}\right)^2\frac{ds}{g_{44}} = \left(g_{44}\frac{dt}{ds}\right)^2\int\frac{ds}{g_{44}} = nh.$$

To a first approximation we have

$$\left(g_{44}\frac{dt}{ds}\right)^2\frac{S}{g_{44}} = nh,$$

where S is the length of the periodic path.

Since S corresponds to the measured time in experimental observations, we have

$$\left(\frac{dt}{ds}\right)^2 = \frac{nh}{g_{44}T},$$

$$T = \text{periodic time.}$$

From the solution of the spatial components of momentum integral we have

$$H\left[1+\frac{\left(\frac{dt}{ds}\right)^2}{H}\right] = \frac{2\pi^2 m E^2 e^2}{n_1^2 h^2},$$

$$n_1 = \text{total quantum number,}$$

or

$$H = \frac{2\pi^2 m E^2 e^2}{n_1^2 h^2}\left[1-\frac{hn}{g_{44}\,.\,H\,.\,T}\right].$$

Moreover, since

$$g_{44} = 1-\frac{eE}{r},$$

we have to a first approximation, since

$$g_{44} = 1-\tfrac{1}{2}H \quad \text{on the average,}$$

$$H = \frac{2\pi^2 m E^2 e^2}{n_1^2 h^2}\left[1-\frac{\gamma n}{h n_1}\right],$$

for

$$HT = \left(2\pi^2\frac{Mm}{M+m}\frac{E^2e^2}{n_1^2h^2}\right)\left(\frac{1}{4\pi^2}\frac{M+m}{Mm}\frac{n_1^3h^3}{E^2e^2}\right) = \tfrac{1}{2}n_1h,$$

using the values of H and T derived for the simple atom

* Eddington, Math. Th. of Rel. p. 86.

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and where γ is a constant which is introduced from the change in the units of T. Therefore

$$H = W[1-\gamma' . W^{1/2} . n] = \text{energy of the electronic orbit,}$$

where

$$W = \frac{2\pi^2 M E^2 e^2}{n_1^2 h^2} = \text{the highest energy level of the multiplet,}$$

and

$$\gamma' = \gamma(2\pi^2 m E^2 e^2)^{-1/2}.$$

The constant γ cannot, however, be determined accurately owing to the indeterminateness of the scalar gauge vector in the quadratic first integral which is determined from the electromagnetic field.

If ν and ν' are the frequencies of two lines of a multiplet arising from the same initial state (or ending in the same final state), then

$$h\nu = H_1 - H_2,$$

$$h\nu' = H_1 - H_2';$$

$$\therefore \quad \nu - \nu' = \frac{1}{h}[H_2' - H_2] = \gamma'(n-n')W_2^{3/2}$$

= frequency difference of two lines of a multiplet where H_2 and H_2' have the same n_1, but different n's.

Thus the frequency separations of the components of the lines of a spectral series of any particular element should vary as $W^{3/2}$, where W represents the highest energy level of the components of the multiplet. Further, the ratio of the frequency separations of the components of any one multiplet should be as the ratio of simple integers, *e. g.* in the triplets of the principal series this ratio is *two*.

Since the values of W for the energy of any one particular level in the optical series for any set of similar chemical elements is nearly constant, the frequency separations of the components of any multiplet should vary as γ' from one element to another similar element. Now the constant γ' should vary as N^2, where N represents the atomic number of the element, so that the frequency difference of the energy levels of similar chemical elements varies as N^2, according to the law which was first stated by Dunz (Sommerfeld, *Atombau u. Spektrallinien*, p. 454).

The case of the fine structure of the H and He atoms as well as that of the X-ray spectra considered by Sommerfeld is a degenerate case of the above considerations where s and t become identical. In this case the space degenerates into a

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three-dimensional spatial manifold and the invariant integrals become the usual quantized action integrals. The theory outlined above applies, on the other hand, only to the optical spectra of the elements with more than one electron, since the constant γ depends on the dynamical properties of the inner core, *i. e.* on the nucleus and the inner electrons. The introduction of the "inner quantum number" n arises through the rotational motion of this inner core with respect to the observer.

The following table contains the computed and experimental frequency differences for the energy levels of the spectra of typical alkaline earth and metals, using the 3/2 power law. The data are taken from the tables in Fowler's Report on Series in Line Spectra. The energy levels of the spectra of the other elements of these families has been computed and compared with the experimental results, the agreement being of the same accuracy except in the case of Ba (non-ionized) which, however, is non-Ritzean in type.

Potassium.

State.	$\Delta\nu$ exp.	$\Delta\nu$ calc.
$m\pi$		
21963·06		
22020·77	57·71	
10285·70		
304·39	18·69	18·29
6001·18		
9·33	8·15	8·32
3930·00		
4·83	4·83	4·34
2778·27		
80·56	2·29	2·86

Calcium (ionized).

$m\delta$		
82089·32		
28·73	60·85	
38900·47		
881·30	19·19	19·8
23017·56		
8·95	8·61	9·0

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Calcium.

State.	$\Delta\nu$ exp.	$\Delta\nu$ calc.	
mp			
33988·7			
4094·6	105·9		
146·9	52·2		
12730·3			
50·2	19·9	19·1	
6777·8			Only the larger separation is calculated, the other component being, according to the theory, a simple fraction of this.
85·6	7·8	7·7	
89·6	4·0		
md			
28969·1			
55·2	13·3		
33·5	22·2		
11556·4			
52·6	3·7		
47·0	5·6	5·6	
6561·4			
59·7	1·7		
56·9	2·8	2·4	
4255·5			
54·0	1·4		
2·2	1·8	1·4	

In conclusion, the writer wishes to express his gratitude to Professor E. P. Adams for his interest and assistance during the writing of this paper, which is a continuation of the paper on "The Motion of an Electric Charge"*.

XXXVII. *On Certain Postulates of the Quantum Theory.* By Dr. D. N. Mallik, *Professor of Physics, Muslim University, Aligarh, India* †.

Summary.

FROM Langrange's equations in generalized coordinates, the general quantum condition is deduced in the form $\int E\,dt = Nh$ (where E is the energy of a radiating system and N an integer, h being Planck's constant).

Taking this as the fundamental postulate of the Quantum theory, Fermat's law of swiftest propagation of light and

* Phil. Mag. May 1925, p. 912.
† Communicated by the Author.

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Planck's postulate regarding the equality between the frequency in a stationary orbit and that of subsequent radiation are deduced.

It is then shown that this equality may be explained as well as the Zeeman and Stark effects by considering the motion as that in a disturbed circular orbit. This suggests a concordance between the Quantum theory and the ordinary wave-theory points of view.

It is then pointed out that both theories fix attention on the mean value of the energy of radiation which can also be shown, on the ordinary Electron theory, to be proportional in some cases at least to the frequency as postulated in the Quantum theory.

1. From Langrange's equations in generalized coordinates, if T, V are the kinetic and potential energies and p's the generalized principal coordinates, we have

$$\Sigma\left(\frac{d}{dt}\frac{\partial T}{\partial \dot{p}}-\frac{\partial T}{\partial p}+\frac{\partial V}{\partial p}\right)dp=0. \quad . \quad . \quad . \quad (1)$$

Multiplying this by dt throughout and integrating with respect to t, we derive, provided we can admit that the order of integration is indifferent,

$$\int\Sigma\frac{\partial T}{\partial \dot{p}}dp+\int\Sigma\frac{\partial(T-V)}{\partial \dot{p}}dp/dt=\text{const.} \quad . \quad . \quad (2)$$

This yields equations of the type

$$\int\frac{\partial T}{\partial \dot{p}}dp=\text{constant}, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

since p's are independent, admitting

$$\Sigma\int\frac{\partial}{\partial p}(T-V)dp\,dt=\delta\int(T-V)dt=0. \quad . \quad . \quad (4)$$

This seems to be reasonable, since the initial and final configurations being prescribed, there is nothing to distinguish, during the integration, between the present operator ∂ and the operator δ of the calculus of variation. In any case, the left-hand side is zero for a closed orbit.

Now in accordance with quantum ideas, we may evidently take (subject to the limitations specified above)

$$\int\frac{\partial T}{\partial \dot{p}}dp=n_p h \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where n_p is an integer and h is Planck's constant, showing the exact relation between classical and quantum dynamics.

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2. Again if E is the total energy of the system

$$2\int \mathrm{E}dt = \int \Sigma\left(\frac{\partial \mathrm{T}}{\partial \dot{p}}\dot{p} + \int \frac{\partial \mathrm{V}}{\partial p}dp\right)dt = \int \Sigma \frac{\partial \mathrm{T}}{\partial \dot{p}}dp + \int \Sigma \mathrm{F}_p\, dp$$

$$= \Sigma \int \frac{\partial \mathrm{T}}{\partial \dot{p}}dp \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

if $\Sigma\int \mathrm{F}_p\, dp = 0$, F_p being the impulse corresponding to p.

This, of course, would be true whenever the displacement is zero while the impulse acts.

Assuming this as a condition in the postulation of quantum theory, we get

$$\int \mathrm{E}dt = \mathrm{N}h \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

from (5) and (6), where N is an integer, since fractional values of the coefficient of h are excluded.

3. It should be noted that equation (3) admits of direct verification in the case of the Bohr model of the hydrogen atom. For this (in three dimensional motion) let

$x, y, z,$ be the cartesian coordinates of the electron,
X, Y, Z those of the nucleus,
r, θ, ϕ polar coordinates of the electron,
R, θ, ϕ polar coordinates of the nucleus.
m, M, the masses of the electron and the nucleus.

$$\therefore \qquad 2\mathrm{T} = (m\dot{x}^2 + \mathrm{M}\dot{\mathrm{X}}^2) + \quad + = m\dot{x}(\dot{x} + \dot{\mathrm{X}}) + \ . \ . \ . \ ,$$

since $m\dot{x} = \mathrm{M}\dot{\mathrm{X}}$, etc.

Hence the equation corresponding to (2) becomes

$$\int\left(\frac{\partial \mathrm{T}}{\partial \dot{x}}dx + \frac{\partial \mathrm{T}}{\partial \dot{y}}dy + \frac{\partial \mathrm{T}}{\partial \dot{z}}dz\right) + \int\left(\frac{\partial \mathrm{T}}{\partial \dot{\mathrm{X}}}\partial \mathrm{X} + \frac{\partial \mathrm{T}}{\partial \dot{\mathrm{Y}}}d\mathrm{Y} + \frac{\partial \mathrm{T}}{\partial \dot{\mathrm{Z}}}d\mathrm{Z}\right)$$

$$= \int(m\dot{x}\, dx + \mathrm{M}\dot{\mathrm{X}}\, d\mathrm{X}) + \quad + \ . \ . \ .$$

$$= \int(m\dot{r}\, dr + \mathrm{M}\dot{\mathrm{R}}\, d\mathrm{R}) + \int(mr^2 + \mathrm{M}\mathrm{R}^2)\dot{\theta}\, d\theta$$

$$+ \int(mr^2 + \mathrm{M}\mathrm{R}^2)\sin^2\theta\dot{\phi}\, d\phi \qquad = \text{constant (8) from (2).}$$

But the last two terms are each of them constant on the principle of angular momentum: therefore from (8), we have

$$\int(m\dot{r}\, dr + \mathrm{M}\dot{\mathrm{R}}\, d\mathrm{R}) = \int \mu\dot{\rho}\, d\rho = \text{const.} = n_3 h \text{ say}, \quad . \quad . \quad . \quad . \quad (9)$$

where

$$\frac{r}{1/m} = \frac{\mathrm{R}}{1/\mathrm{M}} = \frac{\rho}{1/\mu}.$$

And we have the spacial quantum conditions of Sommerfeld.

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4. Accordingly the postulate which serves as the basis of the Quantum theory may be stated in the form $\int E\,dt = Nh$, E being the total energy at any time t.

We have, in fact,

$$\int E\,dt = \Sigma E_r t_r, \quad . \quad . \quad . \quad . \quad . \quad (10)$$

where t = period of the rth radiation, if

$$E_r = h\nu_r = \frac{h}{t_r} \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

in accordance with the quantum theory, E_r being the energy given out during the rth radiation.

5. If this is postulated, the minimum increment (Δ) of $\int E\,dt$,

i. e. $$\{\Delta \int E\,dt\}_{\text{min.}} = h, \quad . \quad . \quad . \quad . \quad . \quad (12)$$

on the understanding, however, that for a permanently stable configuration or orbital motion

$$\Delta \int E\,dt = 0, \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

since E = const., and $\int dt$ = const.

6. Again if Δ is replaced in (13) by δ, where δ is the operator of the calculus of variation, we get $\delta \int E\,dt$ or $\delta \int dt = 0$ (since E is constant in a ray of light during its transmission) which is Fermat's law.

7. If Δ refers to two stationary orbits of a Bohr atom, we shall have also from (12)

$$(E - E')T = h \text{ or } \kappa h, \quad . \quad . \quad . \quad . \quad . \quad (14)$$

where κ is an integer, if during a complete period T, h/T or $\kappa h/T$ quanta of energy are given out ; or

$$(E - E') = \kappa h \varpi \text{ or } h\varpi, \quad . \quad . \quad . \quad . \quad (15)$$

from (14) where ϖ is the frequency in either of the orbits.

8. But if Δ refers to emission of radiation during a complete period of a vibratory system of simple period $1/\nu$ we have, from (12)

$$E - E' = h\nu, \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

which is a postulate of the quantum theory of spectral emission.

9. If, then, radiation is associated with change from one stationary orbit to another, we have from (15) and (16).

$$\varpi = \nu \quad \text{or} \quad \kappa\varpi = \nu. \quad . \quad . \quad . \quad . \quad . \quad , \quad (17)$$

Thus the equation $\kappa\varpi = \nu$ ($\kappa = 1, 2 \ldots$) seems to be deducible from general considerations alone.

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10. The following analysis suggests a further explanation of this equality.

Consider the motion of a particle in a central orbit. The equations of motion are

$$r - r\dot{\theta}^2 = -\lambda/r^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

and

$$\frac{1}{r}\frac{d}{dt}(r^2\dot{\theta}) = 0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

Where $\lambda = e^2\left(\frac{1}{m} + \frac{1}{M}\right)$ for hydrogen atom (Bohr model).

Let the orbit be slightly disturbed according to the scheme

$$r = r_0 + R, \quad \dot{\theta} = \omega + \Omega\ ;$$

we have then for the equation of small oscillation

$$\ddot{R} - R\omega^2 - 2r_0\omega\Omega = \frac{2\mu}{r_0^3}R \quad . \quad . \quad . \quad . \quad (20)$$

from (18), and

$$\frac{d}{dt}(2r_0\omega R + r_0^2\Omega) = 0 \quad . \quad . \quad . \quad . \quad . \quad (21)$$

from (19).

For a circular orbit, $r_0 = \text{const.}$, $\omega = \text{const.}$, $r_0\omega^2 = \frac{\mu}{r_0^2}$; whence substituting we get, since R and Ω vanish together,

$$\ddot{R} + \omega^2 R = 0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

Taking $R \propto \cos pt$ we have $p = \pm\omega$, showing that $\nu = \varpi$ or the frequency of radiation is equal to the frequency of orbital motion, if radiation is due to the harmonic motion set up in the disturbed central orbit.

11. Comparing this with Bohr's theory we gather that a change from one stationary orbit to another is associated with vibratory motion and consequent emission of radiation, so that although the net result is expressible by the equation

$$E - E' = h\nu,$$

the result is attained through oscillation of period $1/\nu$.

12. It is worthy of note that the present analysis gives also the Zeeman and Stark effects.

13. Thus for the Zeeman effect, the corresponding equations of the disturbed orbit will be

$$\ddot{R} - R\omega^2 - 2r_0\omega\Omega = \frac{2\lambda}{r_0^3}R + \frac{H}{\mu}\frac{e}{c}(r_0\Omega + \omega R) \quad (23)$$

$$\frac{1}{r_0}\frac{d}{dt}(r_0^2\Omega + 2\omega r_0 R) = -\frac{He}{\mu c}.\dot{R}, \quad . \quad . \quad . \quad (24)$$

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where e is expressed in electrostatic units, $\frac{1}{\mu}=\frac{1}{m}+\frac{1}{M}$, c=velocity of light, H being perpendicular to the plane of the orbit.

Hence from (24)

$$r_0\dot{\Omega}+\left(2\omega+\frac{He}{\mu c}\right)\dot{R}=0,$$

or

$$r_0\Omega+\left(2\omega+\frac{He}{\mu c}\right)R=0, \quad . \quad . \quad . \quad . \quad (25)$$

since Ω and R vanish together.

Remembering that for undisturbed orbit,

$$r_0\omega^2=\frac{\lambda}{r_0^2}-\frac{He}{\mu c}r_0\omega,$$

this leads to the equation

$$\ddot{R}+\left(\omega^2+\omega\frac{He}{\mu c}\right)R=0, \quad . \quad . \quad . \quad . \quad (26)$$

from (23) and (25), or if

$$R\propto\cos pt,$$

$$p=\pm\omega\pm\frac{1}{2}\frac{He}{\mu c},$$

i. e., if $\Delta\nu$= frequency corresponding to the Zeeman effect

$$\Delta\nu=\pm\frac{1}{4\pi}\frac{He}{\mu c},$$

and $\Delta\nu=0$, when H is in the plane of the orbit.

16. Similarly for the Stark effect the equations of small motion are

$$\ddot{R}-R\omega^2-2\omega r_0\Omega=\frac{2\lambda}{r_0^3}R+\frac{eF}{\mu}\frac{R_0}{r_0}\cos\theta, \quad . \quad . \quad (28)$$

and

$$\left[\frac{1}{r_0}\frac{d}{dt}(r^2\dot{\theta})\right]_{\substack{r=r_0+R\\ \dot{\theta}=\omega+\Omega}}=-\frac{eF}{\mu r_0}R_0\sin\theta, \quad . \quad . \quad . \quad . \quad (29)$$

where F is the electromotive intensity of the exciting field and

$$R=R_0\cos(pt+\alpha),$$
$$\equiv R_0\cos\theta,$$

observing that the radial resolved part of $\frac{Fe}{\mu}$ (which is in the direction of x)$=\frac{eF}{\mu}\cdot\frac{x}{r}$, during finite (steady) motion

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and accordingly for disturbed motion the effective part of this is

$$\frac{Fe}{\mu}\frac{R_0}{r_0}\cos\theta. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (29)$$

Similarly for the other component.

From the second equation (29) on integrating (since $\dot{\theta}=\omega$ in the small terms) we have

$$\frac{1}{r_0}\left[r^2\dot{\theta}\right]_{\substack{r=r_0+R\\ \theta=\omega+\Omega}}=\frac{eF}{\mu r_0}\frac{R_0}{\omega}\cos\theta+(r_0\omega), \quad . \quad . \quad . \quad (30)$$

$$\therefore \qquad \frac{1}{r_0}\left[2r_0R\omega+r_0^2\Omega\right]=\frac{eF}{\mu r_0}\frac{R_0}{\omega}\cos\theta. \quad . \quad . \quad (31)$$

Hence, ultimately, we have

$$\ddot{R}+\omega^2R=\frac{3Fe}{\mu r_0}R_0\cos\theta. \quad . \quad . \quad . \quad . \quad (32)$$

from (28) and (31).

$$\therefore \qquad -p^2+\omega^2=\frac{3Fe}{\mu r_0}.$$

$\therefore$ if $\Delta\nu$ = frequency corresponding to the Stark effect

$$\Delta\nu=\pm\frac{3}{4\pi}\frac{Fe}{\mu r_0\omega}, \quad . \quad . \quad . \quad . \quad . \quad (33)$$

where $1/\mu$ = sum of the reciprocals of the masses of the electron and the nucleus.

14. We are accordingly justified in concluding that when the motion of an electron is changed by the requisite impulse, oscillations are set up, resulting in emission of radiation of the same frequency (on the simplest supposition at any rate) as that of the steady orbital motion. Since the oscillation is associated with radiation of energy, the orbital path gradually changes and the final configuration is again one of steady orbital motion in a new orbit, as postulated in Bohr's theory.

15. Thus the quantum theory by no means precludes the supposition that the transfer of energy actually takes place [by quanta] through the mechanism of vibrations set up as in the wave theory. This is also practically the conclusion otherwise arrived at by Sommerfeld (p. 263, 'Atomic Structure and Spectral lines').

16. Again, writing the equation (12) in the form

$$\Delta\int\frac{Edt}{T}=\frac{h}{T}=h\nu. \quad . \quad . \quad . \quad . \quad . \quad (34)$$

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and remembering that the left-hand side is the mean value of the energy radiated away during a complete oscillation (of period T) we observe that if Δ refers to this condition, the above amounts to the statement that

$h\nu$ = mean value of the energy radiated away during a complete oscillation.

17. The physical meaning of this is that on either theory we can only certainly tell what happens at the initial and final stages of the process of radiation, and also what the mean value of the effect is. For it will be recalled that the explanation of even the phenomena of diffraction on the undulatory theory is virtually based on the theorem that half the *mean* energy of an undulation is equal to the illumination produced.

18. The quantum theory, however, definitely asserts that the mean energy radiated is proportional to the frequency. On the undulatory theory also, the mean kinetic energy or illumination refers to a particular wave-length or frequency and is, so far, ascribed a discrete existence. But a nearer concordance may be reached by identifying the energy of radiation with that given by Larmor's expression, viz. $\frac{2}{3}\frac{e^2}{c}\int f^2\,dt$, if we confine ourselves to a vibrating electron (*e.g.* a Bohr electron vibrating in the disturbed orbit of art. 10). Now if v = velocity (vibrational) of the Bohr electron (in the disturbed orbit), relative to the steady motion, $v = v_0 \sin pt$, say; then

$$\frac{2}{3}\frac{e^2}{c}\int f^2\,dt = \frac{4}{3}\pi^2\frac{e^2}{c}v_0^2\nu.$$

[This makes v_0 an absolute constant, for $\frac{4}{3}\pi^2\frac{e^2}{c}v_0^2 = h$.]

19. It is, of course, easy to see that the equation (7) (art. 2) is really based on two postulates, (1) that the change of energy is impulsive, (2) that the impulsive change of energy or the time integral of energy is atomic.

20. With regard to the second principle (that the time integral of energy is atomic) it recalls the familiar equation $\int i\,dt = (n+n')e$, where i is the electric current and $\int i\,dt$ is the total charge on $n+n'$ ions.

This is, perhaps, more than an analogy, for it seems to be pretty evident, as Jeans has pointed out, that the atomicity of h is associated with the atomicity of e, which has really been accepted so far as a fact without any physical explanation.

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21. With regard to the first, it obviously recalls the well-known equation in Elementary Dynamics, viz., $\int F\,dt$ = change of momentum produced.

Although this equation is always true, its use is practically confined in ordinary Dynamics to the case in which a large force (an impulsive force) acts for a very short time, and in which, therefore, it is not convenient to consider the force and time separately. In strictness, however, this is the more fundamental equation and is, as is well known, the basis of Newtonian Dynamics.

Remembering that h or $h/2\pi$ is of the same physical dimension as angular momentum, as has been pointed out by Jeans, the equation $\int E\,dt = Nh$ as the basis of quantum Dynamics seems to be exactly analogous to the fundamental equation of ordinary Dynamics.

22. In his report on quantum theory Jeans mentions Sommerfeld's theory of an element of action represented by $h/2\pi$ or $h/4$, which serves to explain X-rays, γ-rays, and the photo-electric effect. Without going into the exact form of this theory, it is easily seen that such a theory is *a priori* justified in as much as these phenomena owe their origin to impulses. The present formulation rather aims at calling attention to the fact that just as we are led to the conception of finite forces, from that of impulsive forces, similarly the principle of impulsive change of energy contemplated in the quantum theory and that of a continuous change of energy of classical Dynamics may not be necessarily contradictory, and that we are apparently led to the same mechanism of the propagation of energy on the quantum theory as in the undulatory theory.

XXXVIII. *A new Discussion of Bucherer's Experiment.* *By* G. A. Schott, *F.R.S.**

1. U. Doi † has published an article recently in this Journal with the above title, in which he claims that Bucherer's ‡ well-known experiment decides in favour of a mass-formula for the electron proposed by Doi himself and against the mass-formula of Lorentz—to give it its usual name after the writer who first proposed it. In the course of his article Doi writes (*l. c.* p. 446) : "Now, it may be too

* Communicated by the Author.

† U. Doi, Phil. Mag. ser. 6. xlix. p. 434 (1925).

‡ A. H. Bucherer, *Ann. der Phys.* F. 4, Bd. 28, p. 518 (1909).

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far here to enter into any speculative inquiry as to what disturbing cause should have given rise to these discrepancies. And yet it may be noticed, all the same, that some systematic or other error must have anyhow been inherent to Bucherer's estimation of the effective field-intensities at work." Clearly the very definite criticism of Bucherer's work implied in this quotation requires an answer; so also does the claim that Doi's discussion disposes of the Lorentz mass-formula. If I am undertaking the task of replying, it is for two reasons. In the first place, I was privileged to spend a great portion of an eighteen months leave of absence during 1907–1908 at work in Bucherer's private room in the Physical Institute of Bonn University, thanks to his and Professor Kayser's kind hospitality, at the very time the experiments in question were in progress, and thus was able to discuss the experimental arrangements and difficulties fully with Professor Bucherer. Secondly, soon after my return from Bonn I completed the determination of the path of the Lorentz electron in a field of the type used by Bucherer in his apparatus *, but failed in the attempt to apply this method to the estimation of the effect on the film of the so-called non-compensated β rays, to which Bucherer and myself were agreed in attributing the discrepancy now discussed by Doi, because at that time practically nothing was known about the distribution and intensity of the lines in the magnetic spectrum of radium. Some years ago, thanks to the researches of Danysz and of Ellis, information on this subject had increased so much that a new attack on the problem seemed justified, and therefore one of my pupils, Mr. T. Lewis., B.Sc., worked out a detailed method, which enabled him to specify the point of impact on the photographic film of an electron, projected from the grain of radium fluoride at the centre of Bucherer's condenser with any prescribed velocity in any prescribed direction. Thanks to Bucherer's kindness Lewis was able to measure what was left of the original films during the summer vacation of 1923 at Bonn and to complete his numerical calculations by October, 1924, when his paper was sent to the Royal Society †.

In this article I shall begin with the discussion of Doi's discrepancy and of its cause—the presence of non-compensated β rays—and also of the reasons which led Bucherer to relinquish his original idea of using the complete curve for

* Schott, 'Electromagnetic Radiation,' p. 301 (1912).
† Lewis, Proc. Roy. Soc., A vol. 107. p. 544.

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the test of the various mass-formulæ and to rely on the comparison of the maximum deflexions obtained in experiments with different field-intensities. Then I shall compare Doi's mass-formula with the results of all six of Bucherer's published experiments, supplemented for higher velocities by four experiments made by Neumann by Bucherer's method and remeasured and recalculated by Schäfer *. This comparison affords a rigorous test of the mass-formula for velocities ranging from 0·3 to 0·85 times the velocity of light.

2. *Doi's discrepancy and the compensated β rays.*—The principle and details of Bucherer's method are so well known that no space need be wasted in explaining them. All that need be said is that the usual simple theory, as given for instance by Doi himself, only deals with a single class of electrons, the so-called compensated β rays. These pursue straight paths inside the condenser, owing to the fact that the—let us say downward—electric deflexion just neutralizes the upward magnetic deflexion. If all these electrons were projected horizontally and so traversed the condenser parallel to the plates they would produce a trace on the film of width 0·025 cm., exactly equal to the distance between the plates; but some of them, projected upwards or downwards, pass through in an inclined direction, the extreme ones from the centre of one plate to the edge of the opposite one. In Bucherer's apparatus the radius of the film was nearly twice that of the plates of the condenser, so that the width of the trace due to the compensated β rays should be three times the distance between the plates, viz. 0·075 cm., which is in fact the approximate width of the actual trace near the point of maximum deflexion, *i. e.* at an angular distance of 90° from the direction of the magnetic force. The velocity of the electrons which produce the maximum deflexion is β_0 times the velocity of light, where $\beta_0 = X/cH = \sin\alpha_0$ in Doi's notation; but that of those electrons which produce parts of the compensated ray trace at a distance from the maximum is greater: *e. g.*, at the angular distance α the velocity is β times the velocity of light, where $\beta = \beta_0 \operatorname{cosec}\alpha$. The mass-formula has not been used so far, so that agreement subsists between the different formulæ up to this stage. Both lead to the result that β is unity when $\sin\alpha = \beta_0$, and $\alpha = \alpha_0$, or $\alpha = \pi - \alpha_0$, so that the trace reaches from $\alpha = \alpha_0$ beyond the maximum to $\alpha = \pi - \alpha_0$, *when we confine our attention to the compensated β rays.* In Bucherer's

* C. Schäfer, *Ann. der Phys.* F. 4, Bd. 49, p. 934 (1916).

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experiment no. 15, which has been discussed by both Doi and Lewis and is therefore specially suitable for our consideration, the value of β_0 is given by Bucherer as 0·5154, so that α_0 is almost exactly 31°. Thus the compensated β-ray trace should extend over 118° of the film, and its length should be nearly 16·5 cm., because the radius of the film was about 8 cm. The actual length of the trace is ill-defined, because the ends are much fogged, but it is about 19 cm. On p. 245 Doi calculates that this requires β_0 to be only 0·374, or 27 per cent. less than Bucherer's value, always on the supposition that the entire trace is due to compensated β rays alone and that the non-compensated β-rays are ineffective. Doi attributes this discrepancy to errors in the field-intensities, without giving any other reason for his conjecture. But anyone who knows the apparatus used and the precautions taken, cannot help being convinced that errors of this magnitude are utterly inconceivable. Hence we must look for some other cause for the discrepancy.

3. *The non-compensated β rays.*—These are constituted by electrons which pursue curved paths—approximately parabolas—inside the condenser, because the electric and magnetic deflexions, although in opposite directions, do not neutralize one another completely. Bucherer already in his first paper on p. 519 notes that these non-compensated β rays are mainly responsible for the ends of the actual trace and for the fogging in their neighbourhood; in § 5, p. 526, he discusses their role and on p. 527 writes: "In Übereinstimmung mit der Theorie erstreckt sich ihre Ablenkung z über eine grosse Strecke, so dass ein breites Band entsteht, welches bis zur γ-Linie reicht und nur auf der konvexen Seite ziemlich scharf begrenzt ist. Diese Erscheinung zeigen sämmtliche Aufnahmen in der Nähe des Schnittpunktes der Kurve mit der γ-Linie." Further on he discusses the effect of the non-compensated rays on the maximum deflexion and concludes that the consequent error in the value of e/m_0 cannot exceed one half of one per cent. In view of all this and of his constant reference to Bucherer's paper, it is difficult to understand why Doi omits all reference to the non-compensated rays and uses the ends of the actual trace in his test of the mass-formulæ, when measurements in that region are known to be unreliable.

4. In the paper already referred to Lewis has made a point of studying the non-compensated rays in detail (*l. c.* § 5 to 8) and has summarized the results of his calculations and measurements in a table on p. 560 and a diagram, fig. 3, of which the latter is reproduced here by the kind permission

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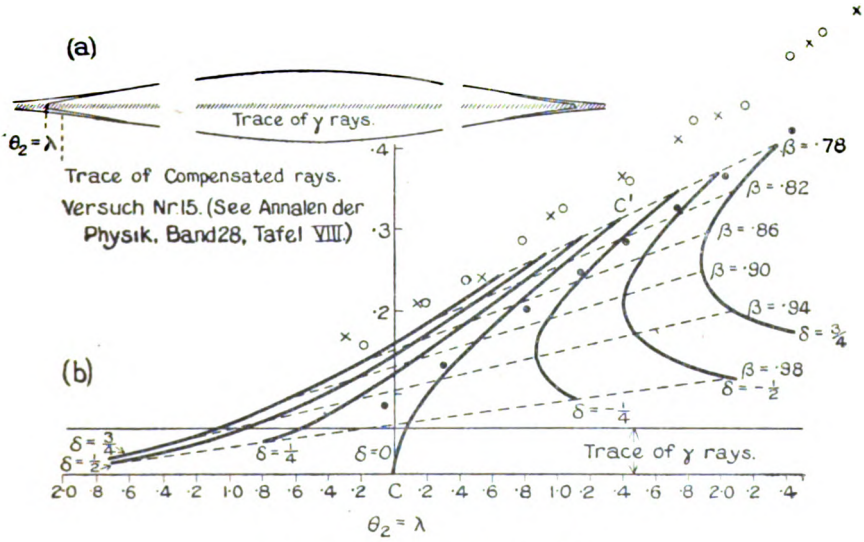
of the Council of the Royal Society. This diagram gives a graphical representation of one of Bucherer's films in the immediate neighbourhood of one end of the actual trace, the value of β_0 being 0·5154. It is uncertain whether this particular film is the one actually taken in experiment no. 15, but at any rate it was taken under exactly the same conditions and gave the same maximum deflexion. The horizontal scale of the diagram, marked along the middle of the undeflected γ-ray line, is about 3·5 times the actual, whilst the vertical scale is 5 times greater still.

The curve CC′ is the middle line of the trace of the compensated β rays calculated according to the Lorentz



[Fig. 3, Proc. Roy. Soc. A, cvii.]

mass-formula, so that the point C is about 31° to the right of the intersection of the film with a diameter of the condenser parallel to the magnetic force, and 59° to the left of the maximum of the trace. The curve CC′ is very nearly parabolic with C as vertex, and accordingly cuts the γ-ray line perpendicularly, as Doi points out on p. 440.

Besides this curve Lewis shows six curves of a family defined by a certain parameter δ, of which family the curve CC′ is one, being defined by δ zero. These curves are drawn as full lines, to the left of CC′ for positive values of δ, to the right for negative values. They approach very close to the γ-ray line at one end and to the curve CC′ at

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the other at large distances from C. Like the curve CC′ itself they are to be regarded as the middle lines of narrow strips or traces, due to pencils of non-compensated β rays; they themselves are produced by electrons passing through the condenser symmetrically along approximately parabolic paths with vertices or turning points halfway between the centre and edge. The parameter δ measures the distance of the vertex below the median plane of the condenser on such a scale that the values $\delta = \pm 1$ correspond to vertices on the plates themselves. The remainder of each strip or trace is due to electrons whose paths deviate slightly from the symmetrical paths, and the number of them falling on an element of the trace of given length diminishes as the numerical value of δ increases; for instance Lewis estimates that the intensity of the traces $\delta = \pm 0{\cdot}75$ is about three-quarters of that of the trace δ zero, whilst their width is about 0·95 as great. These strips may be regarded as filling the whole of the area of the film, but their effect is only appreciable along the trace of the compensated rays, except near its ends, where it extends considerably beyond, to each side, as we see from the diagram.

Besides the family δ Lewis has constructed a second family defined by the parameter β, which denotes the ratio of the velocity of projection of the electron from the radium grain to the velocity of light. The curve β unity coincides with the γ-ray line, whilst the others lie above it in order, rising successively more and more steeply from left to right.

In addition Lewis has represented the readings taken by him of points on the outside edge of the actual trace on film no. 15 near its ends by circles and crosses respectively, each representing the mean of five or six readings, usually differing by less than one tenth of one millimetre. The inner edge of the trace is too much fogged for accurate measurement, but its approximate position is marked by black dots.

The diagram shows that the curves $\delta = \frac{1}{4}, \frac{1}{2}, \frac{3}{4}$, within the range from $\beta = 0{\cdot}78$ to $\beta = 0{\cdot}94$ or $0{\cdot}98$, fall inside the actual trace within a distance of from one to one and a half centimetres, *i. e.* an angular distance of from seven to ten degrees, from the point C, the theoretical end of the trace of the compensated β rays according to the Lorentz formula and Bucherer's values of the field-intensities. Thus there can be no doubt that the presence of such non-compensated β rays in sufficient numbers would be quite sufficient to account for the ends of the actual trace; moreover, such β rays have been observed by Danysz in the magnetic

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spectrum of radium. Consequently Doi's criticism of the Lorentz mass-formula and of Bucherer's experiments becomes pointless; there is no sufficient reason for assuming the presence of large errors of field-intensities in Bucherer's measurements.

Lewis has shown two things: (1) the effect of non-compensated β rays in falsifying the theoretical trace near its ends, so that accurate measurements in that region become impossible, at any rate until we have much more information as to the distribution of intensity in the magnetic β-ray spectrum of radium; and (2) the substantial accuracy of measurements of the trace in the neighbourhood of the maximum deflexion, as already proved by Bucherer in § 5 of his paper. These two results on the one hand demonstrate the soundness of Bucherer's procedure in confining his calculations to the maximum and on the other hand indicate the danger underlying Doi's method of utilizing the whole of Bucherer's curve, just as if each part of it were equally reliable. It is I think quite clear that it is unjustifiable to neglect the effect of the non-compensated β rays at a distance from the maximum.

5. *Doi's Table II.*—Doi lays great stress on the better agreement, as he maintains, with Bucherer's actual curves of those calculated by his own formula as compared with those calculated by the Lorentz formula. Quite apart from the danger already indicated of using the whole of one of Bucherer's for such a comparison, it will be worth while to examine Doi's claim more closely, especially regarding his Table II., because this table deals with Bucherer's curve no. 15, which was considered in detail by Lewis. It seems to me that the arrangement of Doi's tables may lead to a false impression, for my recalculations of some of his figures selected at random indicate that the terms in the same row of the columns headed α, β, z_E and z_D appear to belong together, as do those of columns x and $z_{\text{photogr.}}$, but the two sets of columns do not correspond. For instance, since the radius of the film was 8 cm., as assumed by Doi himself, the value $\alpha = 31°$ corresponds to $x = 8(\pi/2 - \alpha) = 82{\cdot}4$ mm., and not to $x = 95$ mm., which is the value placed by Doi in the same row. In other words, Doi apparently does not compare the calculated and observed deflexions for the same ordinate of the film, which seems to me to be the correct procedure. I have followed this procedure in rearranging Doi's Table II., calculating the values of $z_{\text{photogr.}}$ by interpolating between the numbers given by Doi. The result is shown in Table I. below for some of the values of α used by Doi, and is

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somewhat surprising in so far as the Lorentz formula with this arrangement actually agrees better with Doi's measurements of Bucherer's curve than does Doi's own formula. My recalculations tend to show that Doi's values for both z_E and z_D are a little too low, so that the agreement of the Lorentz mass-formula with Bucherer's curve is quite good from the maximum at $\alpha = 90°$ down to $\alpha = 60°$, that is, for the middle half of the trace.

TABLE I. (Doi's Table II. rearranged.)

α degrees	90.	80.	70.	60.	50.	40.	35.	31.
x mm.	0	13·96	27·92	41·89	55·85	69·81	76·79	82·38
z_E mm.	10·35	9·93	8·75	7·03	4·98	2·80	1·65	0
z_D mm.	10·35	9·87	8·52	6·56	4·28	1·96	0·84	0
$z_{photogr.}$ mm. ...	10·3	9·98	8·93	7·30	5·48	3·53	2·57	1·72

Of course this rearrangement means giving up the attempt to make the end of the theoretical trace at $\alpha = 31°$ fit the end of the actual trace at about 22°, but it seems to me to be more in accordance with the experimental fact of the fogging of the plates near the end of the trace and its probable explanation by means of the non-compensated rays. At any rate the result that the role of the two mass-formulæ can be interchanged by a mere rearrangement of Doi's table, so as to favour the Lorentz formula instead of that of Doi, proves that there is an arbitrary element in Doi's method of comparison. In view of the uncertainty, which unavoidably attaches to the interpretation of Bucherer's curves near their ends, the only sound method is that used by Bucherer himself and his successors, viz. to compare the maximum deflexions obtained with different field-intensities. I shall now apply this method to Doi's formula.

6. *Comparison of Doi's mass-formula with the results of Bucherer and Schäfer.*—For convenience' sake I shall use Doi's notation, but shall distinguish between the two mass-formulæ by using plain letters for that of Lorentz and accented letters for that of Doi. Thus, for example, X and H will denote the electric and magnetic field-intensities as measured by Bucherer and Neumann and used with the Lorentz formula, whilst X′ and H′ will denote the values that must be attributed to them in order to bring Doi's formula into harmony with the experimental results according to his method of calculation. Let us begin by discussing

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Doi's results for Bucherer's experiments nos. 7 and 15, given by him at the foot of his Tables I. and II. on pages 438 and 439.

Doi's expressions on page 436 give for the mass-formula of

$$\text{Lorentz}: \; e/m = (e/m_0) \cos \alpha_0, \quad . \quad . \quad . \quad . \quad (1)$$

$$\text{Doi} \; : \; e/m = (e_0/m_0) \cos^2 \alpha_0'. \quad . \quad . \quad . \quad (2)$$

The factors e/m_0 and e_0/m_0 both represent the specific charge of the resting electron, the value assumed by Doi on p. 446 being $1{\cdot}769 \,.\, 10^7$ e.m.u.

Doi's equations (5) and (6) give, with $\sin \alpha_0 = X/cH$, $\sin \alpha_0' = X'/cH'$,

$$e/m_0 = X/H^2C_E = (c/rH) \tan \alpha_0, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$e_0/m_0 = X'/H'^2C_D = (c/rH') \sin \alpha_0' \sec^2 \alpha_0'. \quad . \quad . \quad (4)$$

These equations hold for the maximum deflexion, given by $\alpha = 90°$, r denoting the radius of curvature of the path of the compensated β ray which produces this part of the trace. Being calculated from the maximum deflexion z and the constants of the apparatus, r is the same for both formulæ, but varies from one experiment to another. Since e/m_0 and e_0/m_0 are also the same, we obtain by comparing (3) and (4)

$$H' \cot \alpha_0' \cos \alpha_0' = H \cot \alpha_0. \quad . \quad . \quad . \quad . \quad (5)$$

We also have $(H'/X') \sin \alpha_0' = (H/X) \sin \alpha_0$; hence

$$X' \cot^2 \alpha_0' = X \cot \alpha_0 \operatorname{cosec} \alpha_0. \quad . \quad . \quad . \quad . \quad (6)$$

7. If all Bucherer's and Neumann's curves existed in their entirety, we could determine α_0' directly from the measured length of the trace, it is true only with a large error, but quite accurately enough for our purpose. Unfortunately most of Bucherer's films are lost, whilst Neumann only used the part near the maximum, so that only two complete curves are available, viz. those used by Doi, nos. 7 and 15. Doi finds for experiment no.

$$7: \; \alpha_0' = 19°{\cdot}1 \text{ instead of } \alpha_0 = 25°{\cdot}35,$$

$$15: \; \alpha_0' = 22°{\cdot}0 \text{ instead of } \alpha_0 = 31°{\cdot}03.$$

From (5) and (7) we obtain for experiment no.

$$7: \; H/H' = 1{\cdot}29, \; X/X' = 1{\cdot}69,$$

$$15: \; H/H' = 1{\cdot}38, \; X/X' = 1{\cdot}90.$$

In other words, in order to bring Doi's formula into approximate agreement with the measured lengths of the traces it is necessary to suppose that Bucherer overestimated his magnetic field-intensities by amounts varying from thirty

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to forty per cent., and his electric field-intensities by amounts varying from seventy to ninety per cent. Not only are these supposed errors impossibly large, but they must vary from one experiment to another, not in a haphazard, but in a perfectly definite manner. Although it must be admitted that the vacuum pumps available at the time of the experiments were much inferior to those in use now, yet the precautions taken by Bucherer to keep his vacuum low and to test it continually were sufficient to exclude large errors in the determination of the electric field-intensity. As regards the magnetic field-intensity the conditions were still more favourable, so that the error could hardly exceed one fifth of one per cent., for the magnetic field was produced by a standardized coil without any iron in its neighbourhood, the currents being kept constant and measured by means of a standardized Siemens precision ammeter.

8. We can however apply a more complete test, and one perhaps more favourable to Doi's formula, if we compromise by assuming that the magnetic field-intensity was measured accurately, so that $H' = H$. Then (5) gives

$$\cot \alpha_0' \cos \alpha_0' = \cot \alpha_0. \quad . \quad . \quad . \quad . \quad . \quad (7)$$

This equation determines α_0' from α_0 and enables us to dispense with the necessarily inaccurate measurement of the length of the trace. We can now calculate l', the length of the trace needed on the present supposition by Doi's formula, and also l, that needed by the formula of Lorentz, and compare them with the measured length, at least for the two films available. We can calculate the electric field-intensities X' and X as before. This procedure amounts to distributing the error between the measurements of the length of the trace and of the electric field-intensity (ur). In this way I have calculated the following table for the five values of β_0 used by Bucherer (the first five rows of the table) and the two values used by Schäfer (the last two rows).

TABLE II.

β_0.	α_0.	α_0'.	β_0'.	l.	l'.	X/X'.	l/l'.	l obs.
0·3173	18° 30′	17° 41′	0·3037	20·0 cm.	20·2 cm.	1·045	0·990	—
3787	22 15	20 53	3570	19·0	19·3	1·061	984	—
4281	25 21	23 29	3985	18·1	18·6	1·074	973	19·8 cm.
5154	31 1	27 58	4690	16·5	17·3	1·099	952	19·0
6870	43 24	37 3	6025	13·0	14·8	1·140	878	—
80	53 5	43 50	69	10·3	12·9	1·16	80	—
85	58 13	47 29	74	8·9	11·9	1·15	75	—

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The last column gives the lengths of the actual traces measured by Doi on films nos. 7 and 15.

This table shows us three things: (1) the error in the electric force needed to bring Doi's formula into harmony with the results of Bucherer and of Neumann, as recalculated by Schäfer, increases to a maximum of about sixteen per cent. as the corrected velocity β_0' increases to the value 0·7; (2) the length of the trace l', calculated from Doi's formula, exceeds l, that calculated from the Lorentz formula, by an amount which increases relatively and absolutely as β_0' increases; (3) the value of l' is still much below the measured value, to judge from Bucherer's experiments nos. 7 and 15, so that the discrepancy pointed out by Doi still exists, though in a slightly mitigated form.

Thus, even if we could admit the possibility of imperfections in the value of Bucherer's and Neumann's experiments just sufficient to account for the hypothetical errors in the electric field-intensities and of just the right amount to explain the very particular law of dependence of the errors on the velocities used, we should not thereby dispose of Doi's discrepancy and should still be compelled to invoke the help of non-compensated β rays to account for the unexplained balance. The Lorentz formula on the other hand needs no such errors in the field intensities; it only requires us to take into account the presence of non-compensated β rays in order to explain the deviations near the ends of the traces, where we know already that measurements are exceedingly unreliable. In view of these facts there does not seem to me to be any sufficient reason for rejecting the Lorentz mass-formula in favour of that of Doi, at any rate for values of β less than 0·8 or 0·85. Nevertheless experiments with improved apparatus are very much to be desired, in order to test the formula in the neighbourhood of and beyond this limit.

XXXIX. *The Two-Stage Transformation of Magnetite into Hematite.* *By* Lars A. Welo *and* Oskar Baudisch *.

(From the laboratories of the Rockefeller Institute for Medical Research, New York.)

We have been engaged during the past year in the study of a certain chemical reaction † in which one of the final products is a magnetic oxide of iron. It is a ferro-ferric oxide of the composition $2FeO, 3Fe_2O_3$. It was

* Communicated by the Authors.

† O. Baudisch and P. Mayer, *Biochem. Z.* cvii. p. 1 (1920); and O. Baudisch and L. A. Welo, J. Biol. Chem lxvi. p. 261 (1924).

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natural to compare its properties, both physical and chemical, with those of the more common ferro-ferric oxide FeO, Fe_2O_3, which is magnetite and usually written Fe_3O_4. At the same time a comparison was made with the oxide of Haber and Kaufmann*, which also has the composition $2FeO, 3Fe_2O_3$, but is made in a different manner. During this work of comparison it was discovered that the process of transformation of each of these ferro-ferric oxides into the non-magnetic ferric oxide Fe_2O_3 takes place in distinct stages, and that the disappearance of the magnetism by heating is dependent on the existence of a preliminary oxidation.

Our work on the intercomparison of the properties of the three oxides is about complete, and a full report on it is to be published. In the present paper we shall be concerned only with the conditions which govern the transformation of each of these magnetic ferro-ferric oxides into the non-magnetic ferric oxides. The conditions are the same for each of them; at least they are qualitatively so. It will be sufficient, for the purpose of this paper, to describe the steps of the transformation of the magnetite, FeO, Fe_2O_3, into the non-magnetic, purely ferric oxide, Fe_2O_3.

Preparation of Magnetite.

The magnetite used in this study was the black, microcrystalline substance formed when a solution containing one mol of ferrous sulphate and two mols of ferric sulphate is poured into a boiling solution of sodium hydroxide. It is necessary that sodium hydroxide be present in excess so as to give, always, an alkaline solution. The precipitate was washed until the filtrate showed no alkali when tested with litmus paper. After collection on a filter the oxide was dried in a desiccator.

The Qualitative Observations.

Generally speaking, the facts observed on heating the oxide in a stream of oxygen are as follows:—The colour of the oxide changes suddenly from black to a dark red at about 220° C.; the oxide remains magnetic, although the iron has been completely converted into the ferric form so that the composition has become Fe_2O_3. The ferricyanide test showed not a trace of Prussian blue, and hence no

* F. Haber and A. Kaufmann, *Z. Elektrochem.* vii. p. 733 (1900–1901).

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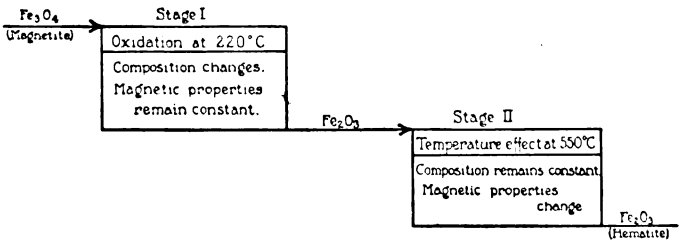
ferrous iron after oxidation for a sufficient time at 220° C. A solution of the oxide in hydrochloric acid titrated with potassium permanganate likewise yielded no iron in the divalent form. All of this shows that Fe_3O_4 may be completely oxidized to Fe_2O_3 at a temperature of 220° C. without loss of the magnetic properties.

On further heating, the oxide, now Fe_2O_3, remains magnetic until a temperature of 550° C. is reached. At this temperature a non-reversible transformation takes place, for the oxide becomes permanently non-magnetic. This transformation is obviously a pure temperature effect, since the oxidation was already complete at the lower temperature of 220° C. But to test the point a sample which had first been oxidized at 220° C. was heated in an atmosphere of nitrogen carefully freed from oxygen. It again became non-magnetic. The necessary condition, however, for the loss of magnetism at 550° C. is that the Fe_3O_4 must first be oxidized to Fe_2O_3 at some lower temperature. If Fe_3O_4 is

Fig. 1.



heated in nitrogen without a preliminary oxidation it is stable, and retains its magnetic properties even if heated to 800° C. These observations are briefly summarized in the scheme shown in fig. 1.

It has been stated that the oxidation begins at 220° C. A more precise statement would be that the oxidation becomes sufficiently rapid at that temperature so that the change in colour may be observed. It is recognized that oxidation may take place at a much lower temperature.

It is interesting to note here that the temperature of stage II. is found to be nearly the same as, and probably does actually coincide with, the Curie point for natural magnetite, which is 525° C., according to Graetz *.

* Graetz, 'Handbuch der Elektrizität und des Magnetismus,' vol. iv. p. 888.

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The Permeabilities.

It was decided to make more precise measurements of the permeabilities on the original Fe_3O_4 and on the derived oxides after each stage of the transformation. A long magnetizing solenoid of two layers was wound on a brass tube. There were 13·6 turns per centimetre, so that the field intensity turns out to be 17·1 gauss per ampere. Another brass tube was made to fit into the tube carrying the solenoid. On this second brass tube circular grooves were cut to make room for test coils of, respectively, 4, 20, and 100 turns. The leads were carried to binding-posts at one end so that any one of the coils could be connected to a high sensitivity Leeds & Northrup ballistic galvanometer. The oxides were packed by jarring (not by tamping) into a glass tube which slipped into the second brass tube. The length of packing was always 20 centimetres, so the demagnetizing factor becomes entirely negligible. The densities of packing could not be regulated, but were never far from an average value of $1{\cdot}32 \frac{\text{gr.}}{\text{cm.}^3}$. The corrected permeabilities μ_c were calculated from the observed permeabilities μ_o by the relation

$$\mu_c = (\mu_o - 1)\frac{1{\cdot}32}{\delta_p} + 1,$$

where δ_p is the density of packing.

The fact that these oxides have permeabilities of about 3 at the most simplifies the procedure. The galvanometer deflexions with oxide in the glass tube and with the tube empty are of the same order of magnitude, and their ratio R, for a given magnetizing field, can be introduced directly into the formulæ.

Let A_o be the internal cross-section of the glass tube containing the oxide, and A_e be the mean area of the test-coil wound on the brass tube.

With the empty tube the flux through the coil is A_eH and the deflexion

$$d_e = CA_eH,$$

C being a constant.

With oxide in the tube the flux is

$$(A_e - A_o)H + A_oB = (A_e - A_o)H + A_o\mu H,$$

so that the deflexion

$$d_o = C[(A_e - A_o)H - A_o\mu H],$$

$$\frac{d_o}{d_e} = \frac{(A_e - A_o)H + A_o\mu H}{A_eH} = R,$$

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giving

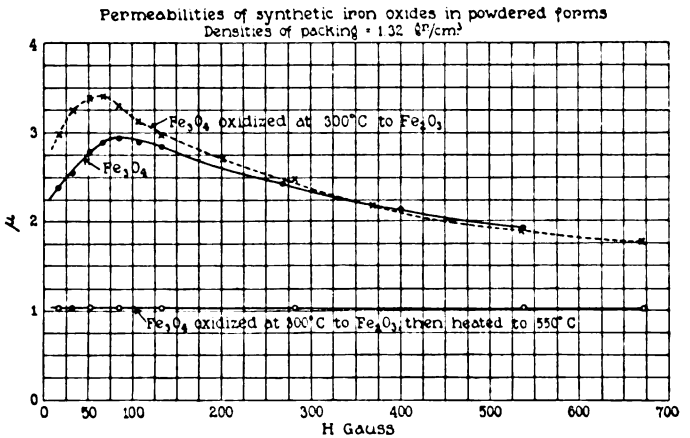
$$\mu = \frac{A_o}{A_e} R - \frac{A_e - A_o}{A_o},$$

and, if we desire, an equally simple derivation of the induction

$$B = \frac{H}{A_o} [RA_e - (A_e - A_o)].$$

Field intensities greater than 85 gauss could not be obtained without undue heating of the solenoid, so that another was used for the stronger fields. It carried several hundred turns. As it was rather irregularly wound it had to be calibrated, and was found to give a field intensity of 134·2 gauss per ampere.

Fig. 2.



The results of the magnetic measurements are shown in fig. 2. Our qualitative observations are confirmed. The maximum permeability of the oxide after having passed the first stage of transformation is somewhat higher than that of the original Fe_3O_4, and there is shown a considerable shift of its position. No reason is known for this. At higher fields the curves coincide, which accounts for our qualitative observation (made with high field intensities) that the magnetic properties remain unchanged on oxidation at a low temperature. After the second stage the permeability is seen to be nearly, but not quite, unity at all fields. The maximum residual permeability is 1·045, and is so small that the material would be considered non-magnetic towards rough qualitative tests.

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The Change in Structure.

The crystal structures of magnetite and hematite are known to be different. Bragg * and Nishikawa † found for magnetite a diamond-point structure, and Davey ‡ found that hematite is like corundum, which, in turn, resembles calcite. It was of interest to determine whether the change of one structure into the other takes place at stage I. or at stage II. It seemed improbable that it changes at stage I. on account of the constancy of the magnetic properties when the oxide passes through that stage. On the other hand, it was difficult to assume that it changes on stage II., for it would involve the assumption that Fe_2O_3 has allotropic forms, and can assume either the form found for magnetite or the calcite structure usually obtained for hematite.

Diffraction patterns of the original Fe_3O_4 and the resulting oxides after each stage of transformation were obtained for us by Dr. Wheeler P. Davey, of the General Electric Company, to whom we herewith express our thanks. The original Fe_3O_4 and the Fe_2O_3 which had passed through stage I. gave identical patterns, and the spacings were the same to within one-tenth of one per cent. The Fe_2O_3 which had been through stage II. of the transformation, however, showed the pattern usually found for Fe_2O_3. The disappearance of the magnetic properties of the oxide is therefore associated with the change in structure taking place at stage II., and is not connected with the change in composition. It is also evident that the atoms of iron and oxygen in Fe_2O_3 have two alternative arrangements in the crystal. If Fe_2O_3 is derived by oxidation of Fe_3O_4 at a low temperature, the Fe_3O_4 structure is retained, and only at a higher temperature of about 550° C. does this structure become unstable and change into the more stable one similar to calcite. The original Fe_3O_4, however, as has already been pointed out, remains stable up to temperatures of at least 800° C. if we prevent oxidation to Fe_2O_3.

This result suggested the interesting problem of finding room for more oxygen in a crystal of Fe_3O_4 without a change in the arrangement of the atoms already in place. We are indebted to Dr. L. W. McKeehan and Dr. R. M. Bozorth, of the Western Electric Company, for aid in this part of the study.

* Bragg, Phil. Mag. xxx. p. 305 (1915).
† Nishikawa, Proc. Math. Phys. Soc. Tokyo, viii. p. 199 (1915).
‡ Davey, Phys. Rev. xxi. (6) p. 716 (1923).

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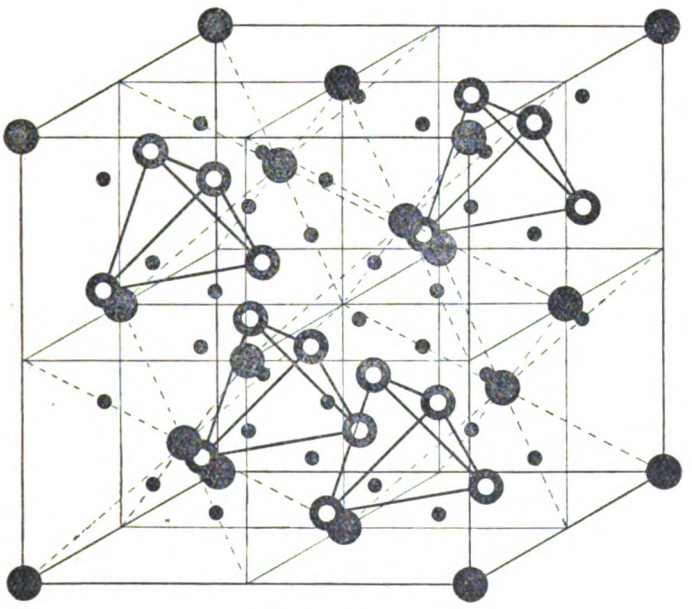
Fig. 3 shows the unit cube for magnetite as constructed from data given by Wyckoff *. The unit cube contains eight molecules, so that Fe_3O_4 may be written $Fe_{24}O_{32}$. After oxidation to Fe_2O_3 the corresponding composition would be $Fe_{24}O_{36}$. We must find room for four additional oxygen atoms in the cube. The first places to suggest themselves are the centres of the tetrahedra formed by the

Fig. 3.



MAGNETITE

trivalent iron atoms, and they are thus shown in fig. 4. In view of the uncertainties as to the actual radii of combination, it is quite possible for the extra oxygen atoms to be placed, as shown, without undue distortion of the system. The edge of the unit cube has a length $a = 8{\cdot}30$ Å., and the distance from the centre of the tetrahedron formed by trivalent iron atoms to each corner is

$$\frac{a}{8}\sqrt{3} = 1{\cdot}795 \text{ Å}.$$

* Wyckoff, Journ. Franklin Inst. cxcv. pp. 531, 544 (1923).

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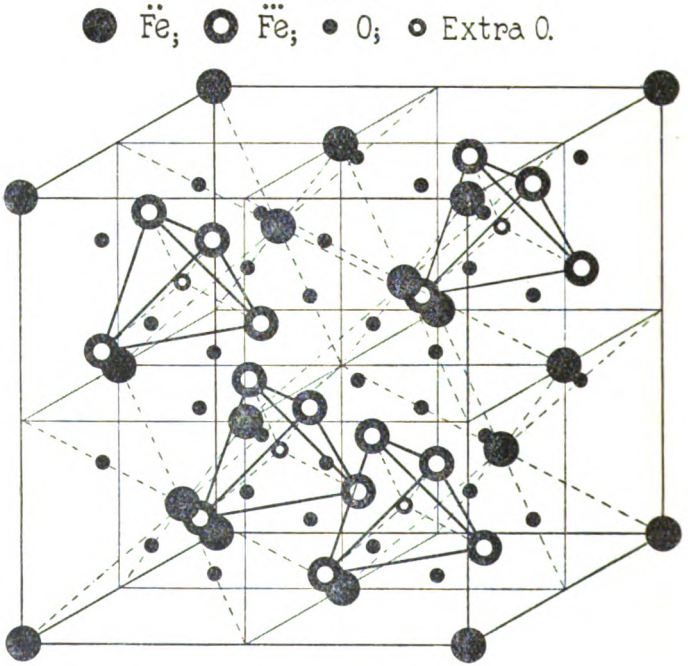
The radius of the oxygen atom is usually taken to be 0·65 Å. This leaves 1·145 Å. as a remainder for the radius of the iron atom. The radius of the iron atom appears to be variable, and values as low as 1·25 Å. have been found in the case of pyrites * and in iron itself.

An alternative and perhaps equivalent arrangement would be to place an oxygen atom at the middle of each edge of the unit cube. The room at our disposal would be the same. This question is not considered here, as it would

Fig. 4.



OXIDIZED MAGNETITE

require a more detailed study of the diffraction pattern, and would probably be indeterminate even then. We are here concerned only with the possibility of putting more oxygen in magnetite so as to change it to hematite without changing the existing arrangement of the atoms.

A few remarks may appropriately be added here regarding an earlier objection to our interpretation which has now no force, since we see that it is possible to convert Fe_3O_4 to

* 'X-Rays and Crystal Structure,' W. H. and W. L. Bragg, 4th Edition, p. 172.

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Fe_2O_3 without disturbing the structure. The contention was made that on the first stage the oxidation was only superficial, and that the cores of the particles remained unchanged. It was supposed that complete oxidation took place only at the higher temperature. The superficial layer of Fe_2O_3 formed, then, on stage I. would form so small a proportion of the whole that the magnetic properties and the diffraction pattern would appear unchanged. The fact that the oxide which has been through stage I. loses its magnetism and changes its structure when heated in nitrogen to 550° C. makes this improbable. The improbability is heightened by the fact that unoxidized Fe_3O_4 remains magnetic after heating in nitrogen to a still higher temperature. The nitrogen cannot contain sufficient oxygen as an impurity to bring about the necessary oxidation. That the oxidation is not superficial is shown also by the chemical tests for ferrous iron, for in these tests the whole particle, core and surface, is first dissolved in hydrochloric acid. To make doubly sure, a test was made for increase in weight when the transformation at stage II. takes place in a stream of oxygen. Instead of the calculated increase of 32 milligrams, for the particular sample used, there was a decrease in weight of about one milligram.

The Order of the Oxidation Process.

We are now in possession of an unforced explanation as to why the presence or absence of magnetism in the synthetic ferric oxide Fe_2O_3 depends on the order in which the chemical operations are carried out. Hilpert * oxidized an existing ferro-ferric oxide into the ferric oxide by means of the strong oxidizing agents H_2O_2 and $K_2S_2O_8$, and found the product to be magnetic. On the other hand, we † have precipitated ferrous hydroxide in the presence of the same oxidizing agents, and the resulting oxide Fe_2O_3 is non-magnetic. The two cases may be represented by

$$(1)\ FeSO_4 + 2NaOH + xO_2 \rightarrow xFe_3O_4 + x\left[\begin{matrix} H_2O_2 \\ \text{or} \\ K_2S_2O_8 \end{matrix}\right] \rightarrow \underset{\text{Magnetic.}}{xFe_2O_3}$$

$$(2)\ FeSO_4 + 2NaOH + x\left\{\begin{matrix} H_2O_2 \\ \text{or} \\ K_2S_2O_8 \end{matrix}\right\} \rightarrow \underset{\text{Non-magnetic.}}{xFe_2O_3}$$

In case (1) the oxide first formed is magnetite, and it retains its structure in spite of the subsequent oxidation to Fe_2O_3. In case (2) the conditions of precipitation are such that the usual Fe_2O_3 structure is built up from the start.

* Hilpert, *Ber. Chem. Ges.* xlii. p. 2248 (1909).

† O. Baudisch and L. A. Welo, Journ. Biol. Chem. lxi. p. 261 (1924).

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Summary.

It is shown that the ferro-ferric oxide Fe_3O_4 (magnetite) can be completely oxidized to Fe_2O_3 at a low temperature of 220° C., so that the maximum permeability may even rise from 2·93 to 3·39, the density of packing of the powders being 1·32 gr./cm.^{3} Then, if this ferric oxide is heated in a neutral atmosphere of, say, nitrogen at about 550° C., the maximum permeability falls to 1·045. The nearly total loss of permeability is therefore purely a temperature effect. But the necessary condition is that the ferrous iron in Fe_3O_4 must first be oxidized to the ferric form. If Fe_3O_4 is not first oxidized, it may be heated in the absence of oxygen to at least 800° C. without permanent loss of permeability.

The change in crystal structure came on the second stage; that is, the oxide Fe_2O_3 had the same structure as the original Fe_3O_4, and did not assume the structure usually found for Fe_2O_3 until the temperature of 550° C. had been reached. An oxide of the composition Fe_2O_3 can therefore have two structures. It is shown that there is room for more oxygen in the atomic arrangement of magnetite without undue strain on the structure. It is pointed out that the results account for the formation of magnetic or non-magnetic ferric oxides according to the order of the chemical operations.

February 20, 1925.

Note added on reading proof.

Our attention has been called to an article by Sosman (Journ. Wash. Acad. Sci. vii. p. 65, 1917), in which he discusses the properties of magnetic ferric oxide, and refers to earlier studies. These studies include that of Hilpert, with which we were already familiar, as shown by our reference. None of these papers, however, bring out the fact that the change in the crystal structure of the oxide and the change from the magnetic to the non-magnetic form take place together.

Since our paper was written we have attempted similar work with natural magnetite. It appears that the transformation at stage I. can be carried out but only at a much higher temperature (about 800° C.). The transformation at stage II. cannot be carried out at any temperature below that at which the Fe_2O_3 begins to decompose. (See Sosman and Hostetter, Bull. Amer. Inst. Min. Eng. cxxvi. p. 930, 1917.)

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XL. *An Extension of the Theorem of the Virial.* *By* Prof. E. A. MILNE *.

THE equations of motion of a particle of mass m at a point (x, y, z) moving under a force whose components are X, Y, Z, are

$$m\ddot{x} = X$$

and two similar equations. Using the identity

$$\frac{1}{2}\frac{d^2}{dt^2}(x^2) = \dot{x}^2 + x\ddot{x},$$

we have

$$\tfrac{1}{4}m\frac{d^2}{dt^2}(x^2) - \tfrac{1}{2}m\dot{x}^2 = \tfrac{1}{2}Xx.$$

Adding together this and two similar equations and summing for a number of particles, we find

$$\frac{1}{4}\frac{d^2}{dt^2}(\Sigma mr^2) = \tfrac{1}{2}\Sigma mv^2 + \tfrac{1}{2}\Sigma(Xx + Yy + Zz),$$

where

$$r^2 = x^2 + y^2 + z^2, \quad v^2 = \dot{x}^2 + \dot{y}^2 + \dot{z}^2.$$

Integrate through a period of time τ, and use bars to denote mean values with respect to the time. Then

$$\frac{1}{4\tau}\left[\frac{d}{dt}(\Sigma mr^2)\right]_0^\tau = \tfrac{1}{2}\Sigma\overline{mv^2} + \tfrac{1}{2}\Sigma(\overline{Xx + Yy + Zz}).$$

If the motion of the system of particles is periodic and τ is a multiple of the period, the left-hand side vanishes. Again, if the system is statistically in a steady state the left-hand side can be made as small as we please by taking τ sufficiently large. In either case we have

$$\Sigma\overline{\tfrac{1}{2}mv^2} = -\tfrac{1}{2}\Sigma(\overline{Xx + Yy + Zz}). \quad . \quad . \quad . \quad . \quad (1)$$

The expression on the right-hand side of (1) was called by Clausius the virial, and the result expressed by (1) under the conditions stated is Clausius's famous Theorem of the Virial, first published by him in English in the Philosophical Magazine †.

It is the purpose of this note to point out that the Theorem of the Virial remains true of the particles are acted on by frictional forces proportional to their velocities in addition

* Communicated by the Author.

† "On a Mechanical Theorem applicable to Heat," Phil. Mag. ser. 4, xl. p. 123 (1870).

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to the forces X, Y, Z. In other words, frictional forces proportional to velocities can be omitted in computing the virial. The proof is simple.

If the particle of mass m is acted on by a frictional force of magnitude kv, the equations of motion are of the type

$$m\ddot{x} = X - k\dot{x}.$$

When this is multiplied by $\frac{1}{2}x$, it may be written in the form

$$\frac{1}{4}\frac{d^2}{dt^2}(mx^2) + \frac{1}{4}\frac{d}{dt}(kx^2) - \tfrac{1}{2}m\dot{x}^2 = \tfrac{1}{2}Xx.$$

Hence, adding three similar equations,

$$\frac{1}{4}\frac{d^2}{dt^2}(\Sigma mr^2) + \frac{1}{4}\frac{d}{dt}(\Sigma kr^2) = \tfrac{1}{2}\Sigma mv^2 + \tfrac{1}{2}\Sigma(Xx + Yy + Zz). \quad . \quad . \quad . \quad (2)$$

On integrating with respect to t as before, we notice that the terms arising from the frictions vanish if the state is steady, or if the motion is periodic and τ is a multiple of the period. Consequently (1) remains true as before. Frictional forces make no explicit appearance in the equation of the virial.

It may be noted that the presence of the frictional forces may alter the state of the system, and so alter the values of $\frac{1}{2}\Sigma\overline{mv^2}$ and of $-\frac{1}{2}\Sigma(\overline{Xx + Yy + Zz})$. But the two remain equal.

In many cases the presence of frictional forces forbids the existence of a steady state, so that the extension of the theorem is of limited application. Its utility will be sufficiently illustrated by the four following examples :—

I. *Forced vibrations.*

The first example is from elementary dynamics, and illustrates the case when the motion is periodic. Consider a particle moving in a straight line under the action of a controlling force $-mn^2x$, a friction $-k\dot{x}$, and an applied force $F\cos pt$. The equation of motion is

$$m\ddot{x} + k\dot{x} = F\cos pt - mn^2x.$$

Whatever the initial circumstances, the motion is known to be ultimately simple harmonic with period $2\pi/p$. Applying the extended theorem of the virial, we have

$$\tfrac{1}{2}m\overline{\dot{x}^2} = -\tfrac{1}{2}\overline{x(F\cos pt - mn^2x)},$$

the means implying mean values through a period. If V denotes the potential energy of the particle in the field

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of the controlling force, T the kinetic energy, this may be written

$$\overline{T}-\overline{V} = -\tfrac{1}{2}F\overline{x\cos pt}, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

which is the expression of the theorem of the virial for forced vibrations. It follows immediately that the average kinetic energy is less than or greater than the average potential energy according as the lag of phase of the particle behind that of the applied force is less than or greater than $\pi/2$. When the phase-difference is $\pi/2$, $\overline{x\cos pt}=0$ and $\overline{T}=\overline{V}$.

It is worth noticing that, once it is known that the motion is simple harmonic of period $2\pi/p$, the equation of the virial combined with the equation of the dissipation of energy determines the amplitude and phase of the vibration. From the equation of motion, on multiplying by $\dot{x}$ and integrating through a period, we have

$$(2k/m)\overline{T} = F\overline{\dot{x}\cos pt}, \quad . \quad . \quad . \quad . \quad . \quad (4)$$

the well-known equation connecting the average kinetic energy with the mean rate of absorption of energy.

The amplitude and phase follow from (3) and (4) on substituting $x = x_0 \cos(pt-\alpha)$ and evaluating the mean values.

II. *Motion of a star-cluster in a resisting medium.*

For a group of particles acted on only by their gravitational attractions, the virial is equal to minus one-half the gravitational potential energy. Let us denote the latter by $-\Omega$ $(\Omega>0)$. As was pointed out by Poincaré * and Eddington †, the theorem of the virial shows that, for a star-cluster in a steady state,

$$T = \tfrac{1}{2}\Omega.$$

When frictional resistances are acting on a group of gravitating bodies, as probably happened during the early history of the solar system ‡, there can be no steady state, but we can extend the above result in the form of an inequality. From (2) we have

$$T-\tfrac{1}{2}\Omega = \frac{1}{4}\frac{d^2}{dt^2}(\Sigma mr^2)+\frac{1}{4}\frac{d}{dt}(\Sigma kr^2).$$

* 'Hypothèses cosmogoniques,' p. 94 (1913).

† Monthly Notices R. A. S. lxxvi. p. 525 (1916). Also Jeans, 'Problems of Cosmogony,' p. 188 (1919).

‡ Jeffreys, 'The Earth,' chap. iv. (1924).

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When Σmr^2 is a linear function of the time, the first term on the right-hand side vanishes. Now, when the rate of evolution (*i. e.* of contraction) is slow, we may adopt a linear approximation for Σmr^2 without serious error. The second term is essentially negative. We have then

$$T < \tfrac{1}{2}\Omega.$$

If W is the total energy of the cluster,

$$W = T - \Omega,$$

and the inequality may be written in either of the forms:

$$T < -W, \qquad -\Omega > 2W.$$

Thus the kinetic energy is less than minus the total energy; the potential energy exceeds twice the total energy. (*Cf.* Eddington, *loc. cit.*) Further, from the equation of the dissipation of energy,

$$\frac{d}{dt}(T-\Omega) = -\Sigma k^2,$$

we deduce, on eliminating Ω,

$$\frac{dT}{dt} = \frac{1}{2}\frac{d^3}{dt^3}(\Sigma mr^2) + \frac{1}{2}\frac{d^2}{dt^2}(\Sigma kr^2) + \Sigma kr^2.$$

The first two terms will be small for slow evolution. Hence $dT/dt > 0$. It follows that the gain of kinetic energy due to contraction exceeds the loss due to friction.

III. *Brownian motion.*

The theory of the Brownian motion, in a liquid, of suspended particles which are large compared with the molecules of the liquid has been worked out in detail by Einstein*. But the extended theorem of the virial permits of the immediate extension of some of the gas-laws to suspended particles in Brownian motion without further consideration.

Each particle, assumed to be spherical, is acted on by a frictional force proportional to its velocity and to the viscosity of the liquid. The precise value of the resistance is given by Stokes's law. But we now see that when the suspension is in a steady state the forces due to viscosity can be left out of account in calculating the virial, and hence the properties of a gas depending on the virial apply as they stand to the suspended particles.

* *Ann. der Phys.* xi. p. 170 (1903); xix. p. 372 (1906).

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We consider the system of suspended particles only. Let P be the part of the pressure on the walls of the containing vessel due to the suspended particles. By a well-known calculation, the contribution to the virial of the forces arising from the walls of the vessel is

$$\tfrac{1}{2}\mathrm{P}\iint(lx+my+nz)\,d\mathrm{S},$$

l, m, n being the direction cosines of the outward normal, and the integral being extended over the walls. If V is the total volume, this is equal to

$$\tfrac{3}{2}\mathrm{PV}.$$

If the concentration is sufficiently small, the contribution to the virial due to pairs of particles in collision can be neglected. If each suspended particle were acted on only by the viscous resistance calculated by Stokes's formula, it would soon be brought to rest, and there would be no steady state. Actually there is another contribution to the force, due to the fluctuations in motion of the surrounding molecules of the liquid, and these suffice to keep the particles statistically in a steady state. It is easily seen that the contribution to the virial of the random part of the resistance is zero. Omitting the systematic part depending on the velocity, by the theorem, we have

$$\tfrac{3}{2}\mathrm{PV} = \Sigma\tfrac{1}{2}m\overline{v^2}.$$

This shows that the partial pressure P of the suspended particles obeys the gas-laws. A similar calculation gives the law of osmotic pressure for dilute solutions in general.

Though frictional forces act on the suspended particles, there is no "dissipation" of their energy. The particles communicate kinetic energy to the molecules in virtue of their motion of translation through the liquid, but this is on the average returned to the particles owing to the irregular motions of the molecules they collide with. As Clausius said, the theorem of the virial is a mechanical theorem applicable to heat, and kinetic energy turned into heat is fully accounted for.

IV. *The pressure of radiation on the molecules of a gas which is in a steady state.*

Consider an enclosure at temperature T containing a gas in a steady state. The enclosure will be filled with black radiation of temperature T, and each molecule will be absorbing and emitting the frequencies corresponding to its energy levels. For a molecule at rest, the absorption of

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energy will be the same in all directions, and emissions will be equally distributed in direction. Thus, on the average, there will be no gain of momentum due to absorptions, and no gain of recoil momentum due to emissions. The molecule experiences no net pressure of radiation.

But for a molecule in motion, the field will no longer be isotropic to an observer moving with the molecule. Radiation will be more intense in the direction opposite to that of the motion. Consequently there will be an excess of absorptions of oppositely moving radiation, and hence a net gain of momentum in a direction tending to reduce the velocity to zero. To the first order in v, the effect is that of a frictional force proportional to v. The absolute value of the force has been calculated by Einstein *. Here, however, we simply point out that the circumstances are analogous to those for Brownian motion †. By the extended theorem of the virial, the effect of the pressure of radiation can be ignored, and thus all consequences of the virial theorem which hold in the absence of radiation hold also when radiation is taken into account.

Trinity College, Cambridge,
April 1925.

XLI. *Optical Screening-Constant Regularities.* By A. C. Menzies, *M.A., Lecturer in Physics, The University, Leeds* ‡.

Introduction.

RECENTLY Millikan and Bowen (1) have applied certain X-ray laws to optical spectra, and in particular have used the relativity-doublet formula $\partial\nu = K(Z-s)^4$ to express the relationship between doublet-separation in wave-numbers (ν) and the atomic number (Z), the screening-constant s having a value which is adjusted. K is a constant varying inversely as the cube of the total quantum-number, and has for $n=2$ (*e.g.* in the innermost Li series-electron levels) the value 0·365. Applied to lithium-like atoms, the screening-constant had values ranging from 2·02 for Li I to 1·86 for C IV.

* *Phys. Zeit.* xviii. p. 121 (1917).
† Einstein pointed out this analogy in calculating the force.
‡ Communicated by Prof. R. Whiddington, F.R.S.

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The same formula was applied to triplets by treating the wider separation as that of a doublet; since in triplets the term-separations have a simple numerical ratio (*e.g.* the *p*-terms of the elements of group II, 2 : 1), taking instead the total separation will merely alter $(Z-s)$ in a constant ratio.

The formula is here applied generally to optical doublets and triplets, a value of s being obtained characteristic of the atom with its valency electron in the particular orbits concerned. Simple numerical relationships are then found between the screening-constants for elements in the same vertical group of the periodic table.

As might be expected, seeing that they have similar electronic configurations, there is a simple connexion between the values of s calculated for the arc spectra of the alkali metals and for the spark spectra of the corresponding alkaline earths. The values of s for the alkaline-earth spark spectra are approximately nine-tenths those belonging to the corresponding elements of the alkali metals, as is shown in Table I. following :—

TABLE I.

Atom.	s.	Atom.	s.	Ratio.
Li I	2·019	Be II ...	1·937	0·96
Na I	7·448	Mg II ...	6·606	0·89
K I	13·03	Ca II ...	11·64	0·89
Rb I.....	26·96	Sr II ...	24·37	0·90
Cs I.....	40·77	Ba II ...	37·19	0·91
Cu I	20·41	Zn II ...	18·24	0·89
Ag I.....	32·92	Cd II ..	29·95	0·91
Au I.....	55·94	Hg II ...	50·8	0·91

The values of s in the above table are calculated from the separations $(2p_2-2p_1)$ for Li I and Be II, and for corresponding separations in the other elements.

There seems also to be a similar relationship holding between the values of s obtained for np orbits compared with $(n+1)p$ orbits for the alkali metals :—

TABLE II.

Element.	s.	s_1.	Ratio.
Na	7·448	7·858	1·055
K.....	13·03	13·57	1·042
Rb	26·96	28·30	1·050
Cs	40·77	42·92	1·053

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In the second column are the values of s calculated from the first separation in the principal series, and in the third column s_1 is that calculated from the second separation—*i. e.* for Li $(2p_2-2p_1)$ and $(3p_2-3p_1)$ respectively.

The above two tables suggest that there is more than coincidence in the values obtained by applying the relativity formula to optical doublets, and so further relationships were sought.

Screening-Constants and Atomic Numbers.

The screening from the nucleus which an electron suffers because of the remaining electrons in the atom will be greater the greater the total number of electrons; and in considering atoms of elements of the same vertical group of the periodic table, it seemed reasonable to test whether the effective screening of corresponding orbits was proportional to the atomic numbers. It was found (2) that the screening-constants were, in fact, nearly linear with atomic number for all the groups tried. The divergence is more marked for small atomic numbers, as would be expected, since other factors than the total number of electrons contribute to the screening-constant; but for sub-groups such as K, Rb, Cs (1 per cent. out), Ca, Sr, Ba ($\frac{2}{3}$ per cent. out), and Mg II, Ca II, Sr II, Ba II (Ra II is 2·3 per cent. out) the divergence is small.

Screening-constants may therefore be usefully employed in arriving at a number of the right order for the separations of doublets and triplets previously unrecognized or unassigned to their atoms. For example, it can be shown that the separations 3815 and 9829 are probably correct for Au I and Hg II respectively, since they give screening-constants in line with those for Cu I and Ag I, and those for Zn II and Cd II respectively. Moreover, their values for s are in the right ratio (see Table I.).

Again, a screening-constant 7·163 for Al II calculated from Paschen's doublet separation (3) is nearly in line with 16·2 and 24·86 for Ga II and In II respectively, calculated from frequency differences found in tables of wave-lengths given by Weinberg recently (4). These frequency differences have enabled the writer to deduce series for Ga II and In II, but they are withheld for experimental confirmation.

It is tempting to extrapolate for the Ra arc separation; the probable value, 64·12, for the screening-constant would indicate about 2800 for the wider separation. The separations and lines at present attributed to this spectrum are unsatisfactory; Hicks (5) finds separations 2050 : 832, and Anslow

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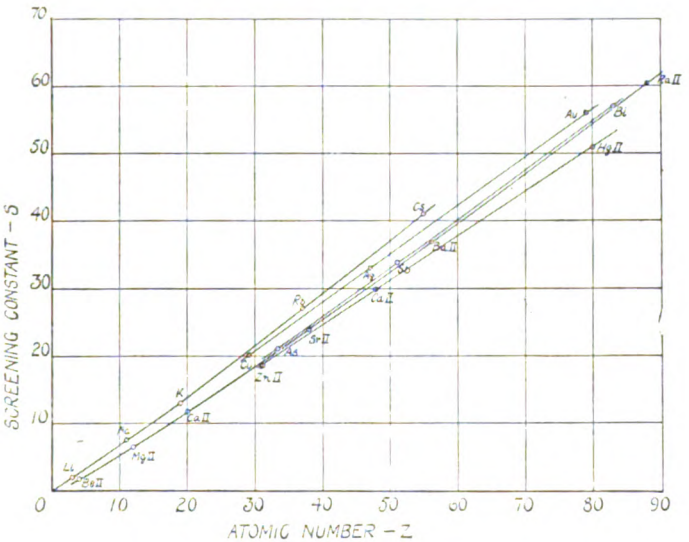
and Howell (6) get 2017 : 1036. These give totals 2882 and 3053. The separation at present regarded as the total separation may in reality be the wider separation.

To show the kind of relation which exists between s and z a graph is given, having atomic numbers as abscissæ, and as ordinates screening-constants calculated as explained above. These curves are to be taken as typical. The alkali-metal curve is for s calculated from the term separations $(2p_2-2p_1)$(Li), and so also is the alkaline-earth spark-line. The curve for As, Sb, and Bi is for screening-constants calculated from the



term separations $(3D_2-3D_1)$ as given by Ruark and others (7).

This curve should really lie much closer to the curve for Sr II, Ba II, Ra II, but it has been raised slightly to show that the two are separate in the reproduction.

It will be observed that all the lines have much the same slope.

Change in S with Building-up of Atoms.

If the elements are considered in the order of their arrangement in vertical groups of the periodic table, they may be imagined to be built up by the successive additions of rings of electrons containing either 8, 18, or 32. Now it is noticeable that for all the groups, increase in the atomic

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number of 8, 18, or 32 corresponds to an increase in s of about 5, 13, and 23. This is well shown by the elements of group I arc, II arc and spark, and III b arc, as in Table III.

TABLE III.

Element.	Z.	dZ.	dS.	Element.	Z.	dZ.	dS.	Element.	Z.	dZ.	dS.
Li I ...	3	8	5·43					Be II ..	4	8	4·123
Na I..	11	8	5·58	Na I...	11	18	12·96	Mg II..	12	8	5·58
K I ...	19	18	13·94	Cu I ...	29	18	12·51	Ca II ..	20	18	12·73
Rb I ...	37	18	13·80	Ag I ...	47	32	23·02	Sr II ..	38	18	12·82
Cs I ...	55			Au I ...	79	(18)	(12·95)	Ba II ..	56	32	23·33
								Ra II ..	88	(18)	(13·12)

Element.	Z.	dZ.	dS.	Element.	Z.	dZ.	dS.	Element.	Z.	dZ.	dS.
Mg II..	12	18	12·18	B I ...	5	8	4·881	C II...	6	8	4·53
Zn II ..	30	18	11·71	Al I ...	13	18	12·07	Si II...	14		
Cd II..	48	32	20·85	Ga I...	31	18	12·06	N III..	7	8	4·24
Hg II..	80	(18)	(11·73)	In I ...	49	32	21·98	P III ..	15		
				Tl I ...	81	(18)	(12·36)				

Element.	Z.	dZ.	dZ.	Element.	Z.	dZ.	dS.
Be I ...	4	8	5·18				
Mg I ..	12	8	5·47	Mg I ..	12	18	12·80
Ca I ...	20	18	13·55	Zn I ...	30	18	12·66
Sr I ...	38	18	13·46	Cd I ..	48	32	22·75
Ba I ...	56			Hg I ..	80	(18)	(12·78)

At the same time the differences illustrate to what extent s is linear with Z. Numbers in brackets have been calculated for an addition of 18 instead of 32 electrons, assuming proportionality.

It will be observed that, for the first two groups, the increments of s cluster round the values 5·4, 13·2, and 23 for additions of 8, 18, and 32 electrons respectively. This suggests that additions of these numbers of electrons in the outer regions of the cores are as effective as a reduction in

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the nuclear charge of amounts given by the values of s above.

Now in the case of a penetrating orbit, we might expect that addition of electrons in the outer part of the core would have most effect in the part of the orbit of the valence electron in this region or outside it. Consequently, since the innermost part of the orbit is approximately the same for different elements in the same column, we can form a rough estimate of the *change* in s to be expected from means in the screening while the electron is in this region and outside it. When eight electrons are added, the difference in s will be 8 for the electron outside the ring, while, if in the ring, the difference would be 3·3.

This gives as an average 5·7, while the average for group I arc and group II spark is 5·2 (these were chosen as being the simplest). Again, for 18 electrons the effective nuclear charge will diminish by 18 while the electron is outside, and by 9·3 while in the region of the ring, giving as an average 13·6. Lastly, for 32 electrons the change to be expected calculated in the same manner is 25.

Such averaging has little physical justification, and has been adopted only in order to gain some estimate of the order of change in screening to be expected. The crude idea of rings has, of course, given way to the more plausible one of separate orbits; but it can evidently still be usefully employed to obtain rough numerical estimates.

Variation in dS *with* n *in the same Atom.*

The greater the penetration of an orbit into the core the less will be the screening, and so the greater will be $(Z-s)^4$, and so the greater also will be the corresponding separation. Deep penetration can therefore be connected with large separations, and small separations can be taken to be a symptom of shallow penetration. (Different orbits of the *same atom* are in mind.) Thus we might expect that if for any atom $\Delta d > \Delta p$, the d orbits penetrate more deeply into the core than the p orbits. Furthermore, the less penetrative the orbit the greater might Δs be, going down a group; for since in the procession from Li to Cs rings of 8, 8, 18, 18 electrons are added in turn, if the valence electron was entirely outside the core all the time, s would change by 8, 8, 18, 18 units at a time respectively. Table IV. shows how s and Δs increase for more distant orbits—*i. e.* as n increases for the same series of terms.

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TABLE IV.

(*a*) Arc Spectra, Alkalies.

Element.	s.	s_1.	Δs.	Δs_1.
Na	7·45	7·858	5·58	5·711
K	13·03	13·57	13·94	14·73
Rb	26·97	28·30	13·80	14·62
Cs	40·77	42·92		

(*b*) Spark Spectra, Alkaline Earths.

Element.	s_1.	s_2.	s_3.	Δs_1.	Δs_2.	Δs_3.
Mg	6·06	10·27	...	5·58	3·68	...
Ca	11·64	13·96	14·65	12·73	13·58	14·42
Sr.....	24·37	27·54	29·07	12·82	12·86	14·48
Ba	37·19	40·4	43·55	23·33	...	27·27
Ra	60·52	...	70·82			

In the above table, s and s_1 apply to $(3p_2-3p_1)$ and $(4p_2-4p_1)$ for Na etc., and s_1, s_2, s_3 to $(3p_2-3p_1)$, $(3d_2-3d_1)$, and $(4d_2-4d_1)$ respectively for Mg etc. The change Δs_2 of 3·68 between Mg and Ca is not in agreement, and suggests that very little penetration occurs in this orbit in the case of Mg, since s_2 for this element is abnormally high.

(*c*) Arc Spectra, Earths.

Element.	s_1.	s_2.	s_3.	s_4.	Δs_1.	Δs_2.	Δs_3.	Δs_4.
Al	7·326	8·726	9·01	9·18	12·07	14·03	14·57	14·78
Ga	19·4	22·76	23·58	23·96	12·06	14·12	14·73	15·06
In.....	31·46	36·88	38·31	39·02	21·98	25·60	26·70	27·39
Tl.....	53·44	62·48	65·01	66·41				

s_1, s_2, s_3, s_4 in the above are screening-constants calculated from the separations $(3p_2-3p_1)$, $(4p_2-4p_1)$, $(5p_2-5p_1)$, and $(6p_2-6p_1)$ respectively in the case of Al, and similarly for the other elements.

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Optical Multiplets are Magnetic rather than Relativistic.

In the foregoing the relativity doublet formula of Sommerfeld has been applied to optical separations, the screening-constant s being used as an adjustable quantity. It has been shown that in passing down a chemical group the screening-constant increases in a way to be expected if the more complex atoms are formed from the preceding ones by addition of rings of 8, 8, 18, 18, and 32 electrons. The formula applied was obtained by Sommerfeld by consideration of the relativity variation of mass with velocity, which will introduce different changes in the energy of orbits of the same total but different azimuthal quantum numbers. There is, however, a large amount of experimental and theoretical evidence derived from a study of the anomalous Zeeman effect to support the view that these multiplet separations are magnetic rather than relativistic in origin, being due to internal atomic magnetic fields.

In the case of a penetrating orbit, the part of the orbit which will contribute most to the relativity effect will be that part where the electron is moving fastest—that is, at the perihelion. This will probably also be true for the magnetic effect, since near the perihelion the electron will be moving fastest, and will therefore be under the influence of greater forces due to the magnetic fields. Thus it is plausible that the screening-constants calculated from a relativity formula should have values in accordance with what is really a magnetic phenomenon.

In its fuller form, K is $\frac{\alpha^2 R}{n^3}\left(\frac{1}{k}-\frac{1}{k'}\right)$, and applies to orbits having the same n's but different k's. In the above it has been applied to orbits having the same n and k but different j's. As used, $K = \frac{\alpha^2 R}{2n^3}$.

It may be noted that an expression of the form $\frac{\alpha R}{n^3}\left(\frac{1}{j}-\frac{1}{j'}\right)$ for K would give correct ratios for the separations if particular values of j were used; but the wider separations would then be associated with the smaller inner quantum numbers instead of with the larger ones. This seems a fatal objection to any such formula. The entering of the j's in the form $(j+j')$, as proportional to the intervals, shows no analogy with the relativity formula.

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Closeness of Agreement.

The numerical relationships outlined above depend upon a fourth-power law. This causes the apparent agreement to be greater than it really is, as, on taking the fourth root of the separation, discrepancies are naturally divided by four.

On the other hand, prophecy is made more uncertain, since a screening-constant which has been predicted for an atom in a particular condition must be raised to the fourth power; and so the expected separation lies within a range which has been multiplied four-fold.

References.

Except where otherwise stated, separations used are those given in
Fowler's Report on Spectra;
Paschen-Goetze, 'Seriengesetze der Linienspektren';
or Hick's 'Analysis of Spectra.'

(1) Millikan and Bowen, Phys. Rev. xxiv. pp. 209-222.
(2) 'Nature,' cxiv. p. 861 (1924).
(3) Paschen, *Ann. der Physik*, lxxi. p. 537 (1924).
(4) Weinberg, Proc. Roy. Soc. A, cvii. p. 138 (1925).
(5) Hicks, Phil. Trans. A, ccxii. p. 64 (1913).
(6) Anslow and Howell, Proc. Nat. Acad. Sci. Wash. iii. p. 409 (1917).
(7) Ruark, Mohler, Foote, and Cherault, U.S. Bureau of Stds. Sci. Paper 490 (1924).
(8) Sommerfeld, 'Atomic Structure,' English edn. p. 76.

Summary.

(1) Screening-constants have been calculated for the optical doublets and triplets of several chemical groups of atoms by application of the relativity doublet formula.

(2) In passing down a chemical sub-group of the periodic table the screening-constant is found to vary directly as the atomic number.

(3) For many such sub-groups the change in s has approximately constant values in passing from one element to the next; for $Z=8$, 18, 32 s is nearly 5, 13, 23 respectively.

(4) These numbers are shown to be of the order to be expected on simple considerations.

(5) The significance of the formula is discussed in the light of the probability that the origin of multiplets is magnetic rather than relativistic.

Physics Laboratories,
The University, Leeds,
May 1925.

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XLII. *Potassium as a Mercury-Vapour Trap.* By A. Ll. Hughes, *D.Sc.*, *and* F. E. Poindexter, *M.A.*, *Washington University, Saint Louis, U.S.A.* *

Introduction.

As is well known, the speed and simplicity of the mercury-vapour condensation pump has led to its almost universal adoption in the production of extremely high vacua. It suffers from the disadvantage that, while it rapidly removes gases and vapours from the vessel to be exhausted, it does not remove mercury vapour. To stop the mercury vapour from diffusing back into the apparatus, the usual practice is to have a trap which can be surrounded by liquid air between the pump and the apparatus to be exhausted. The cost of making liquid air, the difficulty of getting it in certain laboratories, and, in some researches, the need for keeping the mercury trap in action for some weeks without a break, suggested the desirability of looking for some alternative method. The present paper is the outcome of a search for a substitute for liquid air. Years ago, gold-leaf was used to prevent mercury vapour passing a certain point in a vacuum system, but apparently without much satisfaction. During the last two years, we have re-investigated the possibility of metals as mercury-vapour traps. The most surprising result of this investigation is the amazing ability of the alkali metals to absorb mercury vapour. For practical purposes, it is fair to say that the diffusion of mercury vapour past a certain region in a vacuum system is stopped by lining a trap with an alkali metal quite as satisfactorily as by cooling the trap with liquid air.

An account of an investigation on sodium as a mercury-vapour trap has been published by one of us †. In the present paper we give the results of a detailed investigation on the use of potassium as a means for preventing mercury vapour diffusing through a vacuum system. Two methods of investigation were adopted. In the first, we used a qualitative spectroscopic test to determine for how many weeks a lining of potassium inside a tube would remain an effective barrier to mercury vapour. In the second method we used ionization gauges to determine the lowest pressures attainable under our various experimental conditions.

* Communicated by the Authors.

† F. E. Poindexter, Jour. Optical Soc. America, ix. p. 629 (1924).

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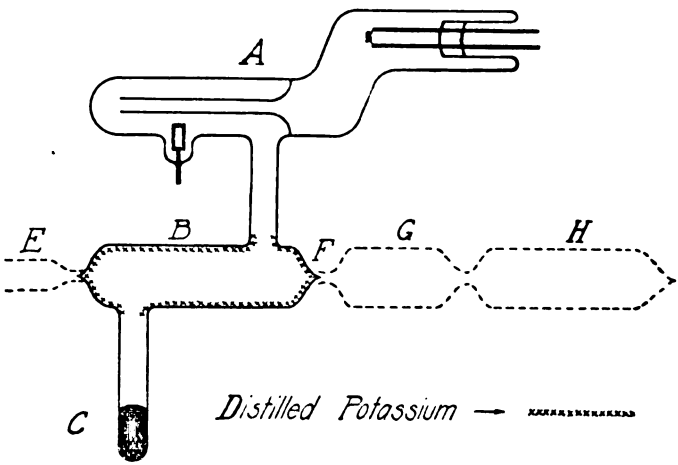
Spectroscopic Tests.

In these tests, use is made of the fact that a small trace of mercury vapour in a discharge-tube is shown by the appearance of mercury lines in the spectrum of the discharge. It has been suggested that, in a mixture of gases, the spectrum of the gas with the highest ionizing potential is relatively less strongly excited than that of the gas with the lowest ionizing potential. It is therefore to be expected that, in a spectroscopic test, traces of mercury would show up more strongly in helium than in other gases. Whether this be true or not, helium has certain other advantages: it is easy to obtain in pure form, and gives a spectrum in which the presence or absence of mercury lines can be determined without ambiguity.

Apparatus.

The apparatus used is shown in fig. 1, which is approximately to scale. It consists of three parts, a discharge-tube, A, the potassium-lined trap, B, and a mercury reservoir, C.

Fig. 1.



The discharge-tube is of the internal capillary type (diameter 3 mm.) which can be viewed end-on. One electrode is a tungsten filament which can be made incandescent to increase the intensity of the discharge if necessary. The mercury reservoir is a tube 11 mm. in diameter and contained 52 grams of mercury. A mark on the outside of the tube indicates the height of the mercury when first put in. The amount which evaporated and had been absorbed by the

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potassium in the course of time could be determined from the depression of the surface of the mercury below this mark. The distance from the surface of the mercury to the horizontal tube B was about 7 cm. The apparatus was connected to a diffusion pump through E. A small piece of newly cut potassium weighing 2·5 grams was inserted into the part H, the end of which was then sealed off as soon as possible. The pumps were then started, and when a good vacuum was obtained the whole apparatus (except the mercury reservoir and the tube H containing the potassium) was heated by a hand blowpipe for about one hour. After cooling, the potassium was first distilled into G and finally into B. When this had been done, G and H were sealed off at F. The potassium was distributed in a thin layer, no doubt unevenly, over the inside of the tube B, the exposed surface area being approximately 30 sq. cm. Owing to slight oxidation on introducing the potassium into the apparatus, the amount of potassium lining the tube B was certainly somewhat less than 2·5 grams, this being the amount of potassium originally put in. A small quantity of helium, purified by passing slowly through charcoal in liquid air, was then admitted to the apparatus, the McLeod gauge showing a pressure of ·01 mm.

Method of Experiment.

The spectrum was excited by a 10,000 volt transformer. During the first few observations it was unnecessary to heat the filament. Soon, however, the tube had hardened to such an extent that it was necessary to make the filament hot to get a discharge to pass. The cause of this diminution in pressure is not known, but we may consider that it made the tests more stringent in that the amount of helium, available for carrying the discharge, was less than before in comparison with possible traces of mercury. The spectrum was examined visually by means of a Hilger constant deviation spectrometer, and a careful search made for the principal mercury lines. The spectrum was also photographed, the exposures being such that the helium spectrum was much overexposed to give every chance for the appearance of mercury lines should there be present any trace of mercury.

Results.

After the apparatus had been sealed off from the pump, the spectrum was examined at frequent intervals (at first

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every week, then less often). Even when the discharge was so strong as to make the helium spectrum very bright, there was not the slightest trace of any mercury lines to be seen, either visually or photographically, until the eleventh week after the tube had been sealed off. Then, and only then, was there any indication of mercury in the spectrum. Along with a very bright helium spectrum, we could see with difficulty the green line of mercury ($\lambda 5461$) but no other mercury lines at all. A photograph, much over-exposed so far as the helium spectrum is concerned, showed the lines $\lambda 4358$, $\lambda 4047$, and $\lambda 3663$, faintly, but nothing of the green line $\lambda 5461$. By this time, the lowering of the level of the mercury in the tube C showed that 3·7 grams of mercury had evaporated and had been absorbed by less than 2·5 grams of potassium. After the eleventh week the mercury spectrum increased very slowly in intensity until the twenty-first week, when the mercury spectrum was plainly visible (this being the last observation made). At this stage, 13 grams of mercury had been evaporated and taken up by the potassium.

This test clearly shows that a comparatively small quantity of potassium spread out in a thin layer acts as an efficient mercury-vapour trap and that it retains its power for a long period. It should be pointed out that this test is unusually drastic in that the source of mercury is very much closer to the trap (7 cm.) than it would be in most experimental arrangements. The amount of mercury vapour diffusing into the trap per second is inversely proportional to the distance from the source to the trap and directly proportional to the cube of the radius (assuming for simplicity that the mean free path of the mercury atoms is greater than the diameter of the tube). This being so, we may reasonably assume that had the mercury been in a tube of the same diameter, but at a distance of say 40 cm. from the trap, it would have taken about a year before traces of mercury vapour would have appeared in the spectrum.

It will be noticed that the potassium continues to act as an efficient barrier to the passage of mercury vapour until it has absorbed over 150 per cent. of its own weight of mercury.

Ionization Gauge Tests.

First Ionization Gauge.

The arrangement used in this test is shown in fig. 2. The path between the ionization gauge and the condensation pump is short and wide so as to give the pump every chance

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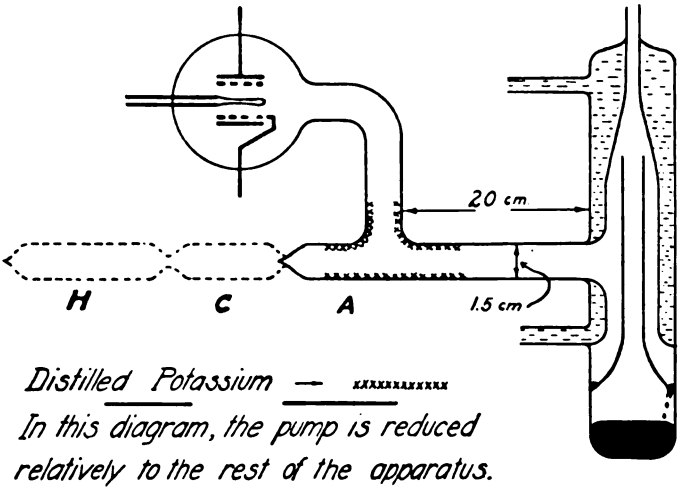
to remove the gases as completely as possible. It also shows what is perhaps as simple and convenient a form of alkali metal trap as can be made. There is no need to describe the ionization gauge as it is of the usual type *. It is sufficient to say that it is a three-electrode tube in which the positive ion current produced by impact of electrons on the residual gas or vapour molecules can be measured. At low pressures, the pressure is proportional to the ratio of positive ion current to the electron current. The gauge was calibrated before this test by inserting a U tube between it and the

Fig. 2.



diffusion pump. The U tube contained a few drops of mercury but not enough of course to close the tube. The U tube was surrounded by melting ice and the ratio of the positive ion current, P, to the electron current, E, was measured with the diffusion pump in action. Under these conditions the only gas or vapour left in the ionization gauge was mercury vapour. According to Knudsen †, the vapour pressure of mercury at 0° C. is $1{\cdot}88 \times 10^{-4}$ mm. We found the ratio of the positive ion current to the electron current with mercury vapour at 0° C to be

$$(P/E)_{0^\circ C.} = 6{\cdot}64 \times 10^{-3}.$$

* O. E. Buckley, Nat. Acad. Sci. Proc. ii. p. 683 (1916). S. Dushman, Physical Review, xvii. p. 7 (1921). F. E. Poindexter, Jour. Opt Soc. America, ix. p. 629 (1924).

† Knudsen, *Ann. d. Phys.* xxix. p. 179 (1909).

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After this preliminary calibration the gauge was set up as shown in fig. 2. A small piece of potassium, approximately 3 grams, was inserted into the tube H and the end sealed off. Then the pump was started and the gauge and connecting tubes (except H) were heated vigorously for an hour or two by a hand blowpipe to drive gases off the walls. Then for a period of two or three hours the anode was outgassed at a red heat by electronic bombardment. Meanwhile the potassium in H was heated at gradually increasing temperatures to drive off gases and then distilled into C and finally into A. The distribution of the potassium is indicated in the diagram. The tubes H and G were now sealed off. The ionization gauge was again outgassed by the hand blowpipe and the anode by electronic bombardment. After cooling, the ratio of the positive ion current to the electron current was again measured and found to be

$$(P/E)^K = 2 \times 10^{-7}.$$

The positive ion current was now so small as to correspond to less than a scale-division deflexion, hence the ratio cannot be determined accurately. However, the vapour pressure of the mercury in the ionization gauge with the potassium trap in action has been reduced to

$$\frac{2 \times 10^{-7}}{6{\cdot}64 \times 10^{-3}} = 3{\cdot}0 \times 10^{-5}$$

times its value at 0° C.

Now, at 0° C. according to Knudsen, the vapour pressure of mercury is $1{\cdot}88 \times 10^{-4}$ mm. Consequently the vapour pressure of mercury in the ionization gauge with the potassium acting as a trap is equal to, or less than

$$(1{\cdot}88 \times 10^{-4}) \times (3{\cdot}0 \times 10^{-5}) = \underline{5{\cdot}6 \times 10^{-9} \text{ mm.}}$$

It should be emphasized that this is an *upper limit*. We do not know that the gas or vapour whose pressure we are measuring is mercury vapour at all, but we do know that if it is all mercury vapour then its pressure does not exceed $5{\cdot}6 \times 10^{-9}$ mm. It is quite likely that, even after the heat treatment we gave to the gauge, minute quantities of gas are slowly being evolved from the walls, anode, and filament, and that what we measure depends on the equilibrium between the rate of evolution of such gases and the rate of removal by the pump. Hence we may justifiably conclude that the efficiency of a potassium trap as a barrier to mercury vapour is such that the pressure of mercury vapour beyond the trap can be reduced to less than 5×10^{-9} mm.

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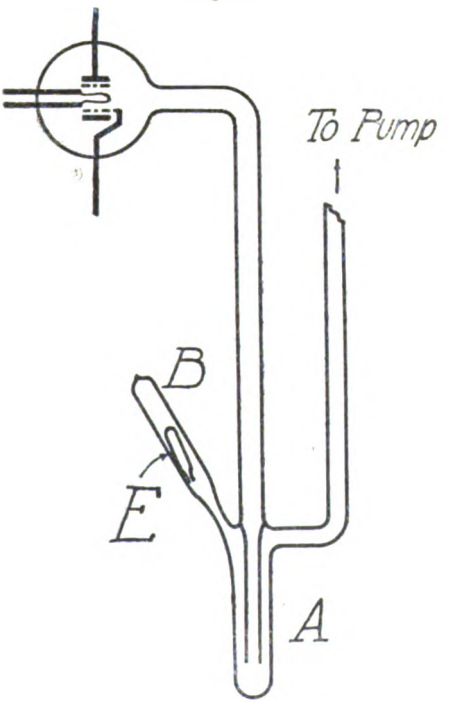
Second Ionization Gauge.

The second ionization gauge was set up in such a way as to enable us to make a direct comparison between the effect of a potassium trap and that of a liquid-air trap. It was also convenient for investigating whether contact of air with the potassium reduced its power as a mercury trap. This apparatus is shown in fig. 3. The tube between the gauge and the trap was 100 cm. long and 2 cm. in diameter, and that between the trap and the pump was 250 cm. long and 1·2 cm. in diameter.

Fig. 3.



The experiments to be described show that a potassium trap is as efficient as a liquid-air trap. The apparatus was outgassed by a hand torch and the anode was made red hot by electronic bombardment for about an hour. Then the part A was surrounded by cold water at 1°·8 C. The ratio of the positive ion current, P, to the electron current, E, was found to be

$$(P/E)_{1^\circ\cdot 8\,C.} = 3\cdot 28 \times 10^{-3}.$$

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(This was not the same ionization gauge as that used in the preceding section.) At 1°·8 C. the vapour pressure of mercury is $2{\cdot}19 \times 10^{-4}$ mm. The next step was to surround A by liquid air, making it into the usual liquid-air trap. The outgassing treatment consisted of heating all the exposed tubes and the gauge itself with a hand blowpipe for a period of one hour and heating the anode to a red heat by electronic bombardment for two hours. After everything had cooled the ratio of the positive ion current to the electron current was measured and found to be

$$(P/E)_{\text{liquid air}} = 2{\cdot}3 \times 10^{-6}.$$

The reduction in pressure is therefore to

$$\frac{2{\cdot}3 \times 10^{-7}}{3{\cdot}28 \times 10^{-3}} = 7{\cdot}0 \times 10^{-4}$$

of its value at 1°·8 C. This gives for the actual pressure a value of

$$(2{\cdot}19 \times 10^{-4}) \times (7{\cdot}0 \times 10^{-4}) = 143 \times 10^{-9} \text{ mm.}$$

The next step was to remove the liquid air and to admit air up to atmospheric pressure into the gauge and pumping system. A small open bottle containing 1 gram of potassium was inserted into B. The pumps were then started and the apparatus was outgassed as before. Heat was applied to the potassium until it melted and ran down into the bottom of A. From here by cautious application of a small flame it was distilled so as to cover the inside of the upper part of A in a thin layer. The outgassing treatment before and after distilling the potassium was carried out in exactly the same way and for the same length of time as was done before and after surrounding the trap with liquid air in the earlier experiment, so as to make the experiments as comparable as possible. After the outgassing was finished the ratio of the positive ion current, P, to the electron current, E, was found to be

$$(P/E)_K = 1{\cdot}2 \times 10^{-6}.$$

Proceeding as before, this gives for the actual pressure a value of

$$\left\{\frac{1{\cdot}2 \times 10^{-6}}{3{\cdot}28 \times 10^{-3}}\right\} \times 2{\cdot}19 \times 10^{-5} = 74 \times 10^{-9} \text{ mm.}$$

These results show clearly that with the kind of outgassing treatment given to the apparatus a potassium trap is at least as good as a liquid-air trap. That it appears to be actually twice as good is no doubt due to the fact that

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the potassium test came *after* the liquid-air test and therefore the apparatus was in a better outgassed condition, even though in between the two experiments air at atmospheric pressure had been admitted to the apparatus for about an hour. We have frequently noticed in the course of our work that a well outgassed apparatus retains much of its outgassed condition even after admitting air to atmospheric pressure for several hours.

After a further outgassing treatment lasting two hours, the pressure dropped to 56×10^{-9} mm.

It should be emphasized again that we do not consider the values here recorded to be real vapour pressures of mercury. They are upper limits, probably many times greater than the true values. They doubtless indicate that, even after considerable outgassing, gas is slowly given off by the walls, anode, and filament, and being removed by the pump. On this view, the lower pressure attained with the first ionization gauge is naturally interpreted as being due to the fact that, on account of the much shorter distance from the gauge to the pump, the evolved gases are removed much more effectively, with the result that a lower equilibrium pressure is attained.

Effect of Admitting Air.

As it is suggested that in many investigations requiring a high vacuum an alkali metal may be used instead of liquid air as a mercury-vapour trap, it is necessary to examine how sensitive the potassium surface is to the effect of gases, and, in particular, to dry air and ordinary air. It is of course obvious that the practical usefulness of potassium as a mercury-vapour trap would be much diminished if exposure to a trace of air destroyed its trapping power. The following tests were carried out.

First Air Test.

Air was passed slowly through phosphorus pentoxide into the apparatus until atmospheric pressure was obtained. About two litres of air at atmospheric pressure passed by the potassium. The effect of the dry air on the surface of the potassium was very marked. The silvery bright surface immediately turned black when air was admitted. After contact with the dry air at one atmosphere pressure for one hour, the air was pumped out again to a pressure below the limit of the McLeod gauge. Next morning the dull black surface of the potassium had become grey and granular. The pump was started again, and the gauge

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and tubes were now outgassed by heating with the hand blowpipe for twenty minutes, and the anode raised to a red heat by electronic bombardment for thirty minutes. The potassium was of course not heated in any way. The pressure obtained after everything had cooled was 38×10^{-9} mm., and after ninety minutes of continuous pumping it fell to 28×10^{-9} mm.

Second Air Test.

Without renewing the potassium surface in any way, the procedure in the first test was again repeated. Dry air was admitted to atmospheric pressure, and, after one hour, it was pumped out again. Next morning the pump was started, and the outgassing consisted of electronic bombardment of the anode for one hour, but without heating the glass with the blowpipe. The pressure obtained was again 28×10^{-9} mm.

Third Air Test.

The sequence of operations here was exactly the same as in the second test, and the pressure obtained was about 30×10^{-9} mm.

Fourth Air Test.

We now admitted room air without any special drying, and left it in for thirty minutes before beginning to pump it out. Then the apparatus was heated by a blowpipe flame for thirty minutes and the anode by electronic bombardment for two hours. The pressure reading obtained immediately after this was 210×10^{-9} mm. Next morning, without any further treatment beyond outgassing the anode by electronic bombardment for one hour, the pressure was found to be 60×10^{-9} mm. The blowpipe flame was now played over the ionization gauge and tubes for thirty minutes, with the result that the pressure fell to 30×10^{-9} mm.

It is to be noticed that the final pressure obtained at the end of the fourth air test was practically as low as that obtained at any time during or before the admission of air. In the course of these tests approximately eight litres of air (six litres of dry air, two litres of room air) were passed over the same potassium surface without affecting its efficiency as a mercury-vapour trap. This is somewhat surprising, as one might reasonably have expected the dull coating formed over the potassium surface to destroy its ability to take up mercury vapour.

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Fifth Air Test.

To examine further the effect of room air as contrasted with dry air, the following test was made. Room air was admitted to atmospheric pressure, allowed to stand for about half-an-hour, and pumped out again. This procedure was repeated three times, so that altogether about six litres of room air had passed over the potassium surface. The apparatus was then pumped out and left overnight. Next day, the potassium was heated for a short while to re-distribute it over the inside of the trap. The outgassing of the gauge and connecting tubes consisted in heating them with the blowpipe flame for thirty minutes and heating the anode by electronic bombardment for about one hour. After this, the pressure gradually fell to 10×10^{-9} mm., the lowest yet obtained with this gauge.

Sixth Air Test.

Most of the foregoing pressure measurements were made on the morning following the day on which the air was admitted. It is desirable to put on record a result which shows the effect obtained when the procedure is hurried. Room air was admitted to atmospheric pressure and allowed to stay for about an hour. It was then pumped out, and as soon as the pressure was hardly noticeable on the McLeod gauge, the potassium was redistributed in the trap by heat, and the gauge and the apparatus were outgassed by the hand blowpipe for fifteen minutes and the anode was brought to a red heat by electronic bombardment for ten minutes. The ionization gauge soon afterwards showed a pressure of 115×10^{-9} mm., this observation being made within thirty-five minutes from the time the diffusion pump came into action. The pressure fell slowly as the pumping proceeded. No doubt it would have reached as low values as were obtained in previous tests, had the apparatus been given further outgassing treatment, but this was not actually demonstrated at the end of this particular test.

Attention is called to the fact that the same one gram of potassium was used in all these tests, and that its power for trapping mercury was not in the least impaired by the passage over it of about twelve litres of air in all. In fact, at the completion of all these tests, the apparatus was opened, and certain alterations made in preparation for an entirely different research. The apparatus was then sealed and exhausted and outgassed, and a pressure of 10×10^{-9} mm. was obtained. The same one gram of potassium was used as in the previous tests, it was merely

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redistributed in the trap by heating with a flame for a minute or two.

Discussion.

Extrapolation of the mercury-vapour pressure curve down to the temperature of liquid air would yield a value of the order 10^{-15} mm., an immeasurably small value. Yet when a liquid-air trap was used between the second ionization gauge and the pump, there was an apparent mercury-vapour pressure of 143×10^{-9} mm. This is certainly not due to mercury, so that in all probability it is due to the insufficient outgassing of the apparatus. The point of this investigation then is that, given the same degree of outgassing of the apparatus, fully as low a pressure can be obtained with a potassium trap as with a liquid-air trap. From the results with the first ionization gauge we may conclude that, with a potassium trap, the pressure of mercury vapour beyond it cannot exceed 5×10^{-9} mm., and may be many times less. We cannot of course say, without further investigation, that, with more strenuous outgassing, a potassium trap will be the equal of a liquid-air trap. Such a test would call for electronic bombardment of the anode and baking the gauge and connecting tubes in a suitable oven for a period of many hours or even days.

The spectroscopic experiments described at the beginning of the paper show that the power of potassium to act as a mercury-vapour barrier lasts for many weeks, in fact, until the potassium has taken up much more than its own weight of mercury. We did not carry out a similar test with an ionization gauge as that would have taken too long a time. One of us * used a sodium trap with an ionization gauge in a former research, and found that its effectiveness as a mercury-vapour barrier was very nearly as high at the end of a twenty-five day period as at any time before that.

The question arises as to whether the use of alkali metals might not be limited by the small but finite vapour pressure of the alkali metals themselves. Scott † has measured the vapour pressures of cæsium and rubidium, and from the empirical formulæ which he gives we may deduce that the vapour pressures at room temperature (say 300° K.) are respectively $5{\cdot}6 \times 10^{-6}$ and $2{\cdot}0 \times 10^{-7}$ mm. From these values one would not expect the vapour pressure of potassium at room temperatures to be much below 10^{-8} mm.

* F. E. Poindexter, Journ. Opt. Soc. America, ix, p. 629 (1924).
† D. H. Scott, Phil. Mag. xlvii. p. 32 (1924).

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Yet the lowest value which we obtained for the pressure with the first ionization gauge was 5×10^{-9} mm. This is calculated on the assumption that the gas left is mercury vapour, since the gauge constants for other gases have not been determined and are not the same as that for mercury, though of course of the same order. We are inclined to believe that the values of the vapour pressures of the two alkali metals given by Scott are too high. Scott states that the pressure of mercury vapour passing a trap surrounded by CO_2 snow ($-50°$ C.) is as much as $1{\cdot}84 \times 10^{-4}$ mm. In an unpublished research by one of us (F. E. P.) on the vapour pressure of mercury at low temperatures, it was found that the pressure of mercury vapour passing a trap at $-50°$ C. was 2×10^{-7} mm., a value to be expected from the vapour-pressure curve. This is much smaller than Scott's value, and suggests some error in his method whereby his values are too high.

One of us (F. E P.) is carrying out a systematic investigation of the vapour pressures of mercury-sodium and mercury-potassium amalgams as a function of the concentration of the mercury.

We have been informed by Mr. P. Lowe of Queen's University, Kingston, Canada, that he has found it advantageous to substitute sodium traps in place of liquid-air traps in an investigation which he has completed on intensities in the hydrogen spectrum. In this investigation, which is probably typical of many, mercury lines in the spectrum could not be made to disappear until several days after liquid air had been placed around the traps, if the mercury vapour had once had access to the electrodes and the part of the apparatus where the spectrum was produced. To avoid this it was necessary to keep the traps continuously in liquid air, a rather costly procedure with a research lasting some months. Mr. Lowe found that about one gram of sodium in each trap acted as a satisfactory mercury-vapour barrier for the three months necessary to complete his observations.

Note on Technique.

As the main interest of this investigation is its practical application, it will not be out of place to offer a few remarks on the technique.

Any alkali metal may be used. Theoretical considerations lead us to expect that the trapping action would be most efficient with that metal having the highest heat of dilution

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with mercury. Actually, however, we are limited in choice to sodium and potassium as the other alkali metals are rare and very expensive. As to sodium and potassium, sodium has the advantage in cost, but since we have found that a very small quantity of potassium retains its activity unimpaired for many weeks, the extra cost of the potassium is not a serious consideration. Sodium has also the advantage that its own vapour pressure is less than that of potassium. We have shown in this paper, however, that even with potassium a pressure of the order of 5×10^{-9} mm. can be obtained, and this is probably due to insufficient outgassing rather than to the potassium. Consequently it is only in the unexplored region of pressures below 10^{-9} mm. that the vapour pressures of the metals may possibly become a deciding factor in choosing between them. We are inclined to believe the vapour pressures of both metals at room temperatures are considerably below 10^{-10} mm. On account of the rapid change of vapour pressures with temperature, cooling the trap with ice would reduce the vapour pressure of the metal by a factor in the neighbourhood of ten as compared with its value at room temperature. This is regarded as a needless refinement, and it is not suggested as at all necessary in using the sodium or potassium as mercury-vapour traps. Potassium has the advantage that, owing to its lower melting and boiling points, it is decidedly easier to handle in pyrex glass apparatus.

We have developed a technique in preparing the sodium or potassium which may be helpful to others who may want to use one of these metals as a mercury vapour trap. The oil in which the sodium or potassium is supplied commercially occasionally contains a constituent which, if the metal is insufficiently washed with pure benzol or some such solvent, may be introduced into the vacuum system along with the metal, and may give a great deal of trouble in preventing the attainment of very high vacua. We have occasionally had to discard a complete system of pump, McLeod gauge, trap, and ionization gauge because of the accidental admission with the metal of this unknown substance, probably a hydrocarbon of high boiling-point. Consequently, we have developed a satisfactory method of cleaning and outgassing a large quantity of sodium or potassium and storing it in small glass tubes.

The technique of preparation is shown in fig. 4. A quantity of the metal amounting to four ounces or more is introduced straight from the bottles in which it was

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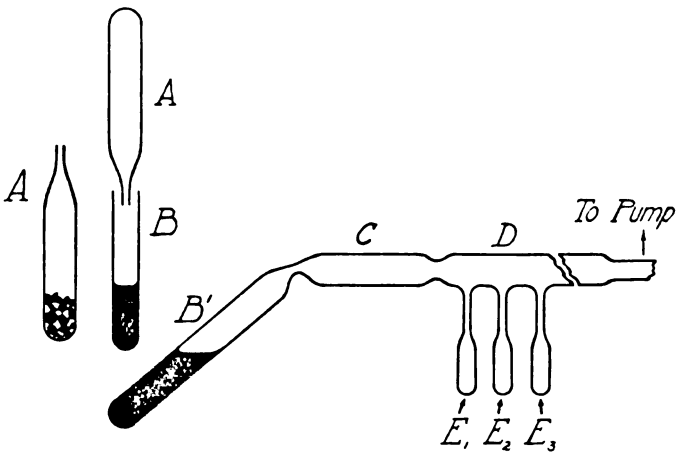
purchased into a pyrex glass tube, about 3 to 4 cm. wide as shown in A. The upper part is drawn down to a width of about 5 mm. Then the metal is heated by a bunsen flame. As the heating is gradually increased the volatile hydrocarbons come off first and burn at the opening, then the heavier hydrocarbons. The heating is slowly increased until the metal itself begins to evaporate and condenses a little higher up the tube. At this stage, when all volatile impurities have been driven off, the tube is allowed to cool, but before the liquid begins to solidify it is poured into another pyrex glass tube B and allowed to solidify at the bottom. Most of the oxide etc. is left behind in A. B is then sealed on to a pumping system in

Fig. 4.



the position B′. The tube D has fused to it a dozen or more thin-walled glass tubes about 2 cm. long and 1 cm. in diameter and with necks of 4 mm. internal diameter. (These are the tubes in which the cleaned metal is ultimately stored.) When a vacuum has been obtained, the lower part of B′ is heated for a long time. The metal evaporates, condenses on the upper part of the tube B′ and runs down again, the action being that of a reflux condenser. At first large quantities of gas are evolved, but after several hours heating very little comes off. Then by heating the whole of B′ the metal is driven into C, and B′ is sealed off. Next the metal is liquefied in C, and by tilting the apparatus to the right (a flexible connexion between the apparatus and the pump allowed this) the metal flows

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to D and fills all the small tubes E_1, E_2, etc. as it passes over them. These tubes are then sealed off in turn. In this way one can in two days or so prepare a sufficient stock of clean outgassed sodium or potassium which will be ample for several vacuum systems, as ordinarily used, for more than a year. The procedure is not so complicated as it seems, and is far preferable to inserting a piece of new potassium which has not been outgassed and which may carry a trace of heavy oil in with it enough to give trouble in the apparatus. Fig. 3 illustrates the way in which these small tubes are used. When the apparatus is assembled, a small tube E holding the potassium is opened and inserted into B, which is then sealed up at the open end. As soon as a good vacuum is obtained, the metal is liquefied by heat and runs down into A.

The shape of the tube on the inside of which the metal is finally distilled may be of many forms. Perhaps the right-angled joint in fig. 2 is as easy to make and as satisfactory as any.

If at any time one suspects that the metal is not acting as well as it should, redistribution of the metal by heating one part and then another of the trap for a minute or two will be found efficacious. It is our experience that this is seldom necessary, even when the surface of the metal is quite dull.

Summary.

(1) A liquid-air trap is almost universally used as a means for preventing mercury vapour diffusing back into a vacuum system from a mercury pump. It has been found that a trap lined with distilled alkali metal is as satisfactory a barrier to the passage of mercury vapour as a liquid-air trap. Any alkali metal may be used. Considerations of cost, however, practically limit one to either sodium or potassium.

(2) In this paper, we give a detailed investigation of the power of potassium (distilled so as to form a lining inside the trap) to stop mercury vapour passing back into the space to be exhausted. An ionization gauge was used to measure the residual pressure of mercury vapour. Using liquid air alone to trap the mercury vapour, the residual pressure in the ionization gauge after outgassing it by heat was $1{\cdot}4 \times 10^{-7}$ mm. The residual pressure, obtained on substituting a potassium-lined trap for the liquid-air trap, after precisely the same heat treatment, was ${\cdot}74 \times 10^{-7}$ mm. These values are not regarded as residual

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mercury-vapour pressures, they indicate that gases are being slowly evolved owing to insufficient outgassing of the apparatus. The lowest residual pressure obtained with a potassium trap after a more thorough outgassing of the ionization gauge and connecting tubes was 5×10^{-9} mm. It is probable that even this value is to be attributed to insufficient outgassing of the apparatus rather than to a genuine residual mercury-vapour pressure. In any case, we can regard it as the upper limit to the vapour pressure of mercury in a vacuum system beyond a potassium-lined trap.

(3) Several litres of moderately dry air may be passed over the potassium surface, making its surface a dull black without appreciably affecting its trapping power for mercury.

(4) Using the first appearance of mercury lines in the spectrum of helium at a pressure below ·01 mm. as a criterion, it has been found that a potassium-lined trap will act as a barrier to mercury vapour until the potassium has absorbed at least 150 per cent. of its own weight of mercury.

Washington University,
Saint Louis, U.S.A.,
May 17, 1925.

XLIII. *Note on a Method of Comparing Inductance and Capacity.* By T. B. Vinycomb, *M.C., M.A., Physics Department, Woolwich Polytechnic* *.

In the January number of the Philosophical Magazine, Professor Ganguli gives his experience in the use of the method proposed by Professor Forsythe in the 'Physical Review' of June 1913 for the comparison of a Self Inductance and a Capacity. He begins by quoting Professor Forsythe's theory. While the deduction is formally correct, the method of proof conceals to some extent the principle of the measurement.

On referring to the diagram in Professor Ganguli's paper, reprinted below, it is seen that a Wheatstone Bridge network is used, three arms of which are formed by non-inductive resistances, and the fourth arm is composed of a self inductance L and a capacity C, connected in parallel, each

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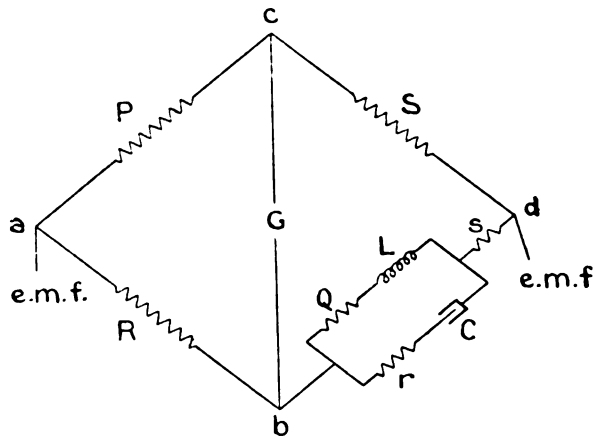
in series with a separate resistance. Another resistance is placed in the arm in series with both, as in the figure.

It is clear that a balance cannot be obtained under these conditions with alternating current, unless this arm is non-reactive, *i. e.* behaves as a pure resistance. The use of the bridge network, in fact, is merely for the purpose of determining when this condition is fulfilled. Any other method can be used by which it is possible to decide when the power factor of the arm is unity.



Let the impedance of this arm, neglecting s for the moment, be Z.

Then

$$\frac{1}{Z}=\frac{1}{Q+jpL}+\frac{1}{r+\frac{1}{jpC}}$$

$$=\frac{(Q+r)+j\left(pL-\frac{1}{pC}\right)}{\left(Qr+\frac{L}{C}\right)+j\left(pLr-\frac{Q}{pC}\right)}.$$

This will be equivalent to a resistance alone, if

$$\frac{Q+r}{Qr+\frac{L}{C}}=\frac{pL-\frac{1}{pC}}{pLr-\frac{Q}{pC}}, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and this condition will be independent of p if

$$Q=r. \quad . \quad . \quad . \quad . \quad , \quad . \quad . \quad . \quad . \quad (2)$$

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Equation (1) leads to

$$LCp^2 = \frac{Q^2 - \frac{L}{C}}{r^2 - \frac{L}{C}},$$

so that for any values of Q and r, both greater or both less than $\sqrt{\frac{L}{C}}$, the arm is non-reactive for a particular value of p. This value becomes indeterminate if

$$Q^2 = r^2 = \frac{L}{C}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

as can also be seen by inserting (2) in (1) above.

Then $$Z = Q,$$

and the impedance for all frequencies is equal to the direct current resistance of the arm. The value of Q includes the resistance of the inductance L. There is no need to "swamp" this resistance as suggested by Professor Ganguli. When the condition

$$Q^2 = r^2 = \frac{L}{C}$$

holds, there is no need for the resistance s in the arm except to obtain a balance on the bridge. It is otherwise a disadvantage, as it reduces the sensitiveness. It should therefore be omitted, and the balance obtained by varying S. The balance does not depend on using equal ratio arms P and R, and any ratio may be used which is found convenient. If equal arms are used, it is easy to maintain the D.C. balance by making equal changes in Q and S. It may be noticed that the resistance required for A.C. balance is that which makes the circuit L, C, Q, r just aperiodic.

I have used this method for the measurement of Inductances between ·15 and ·0005 henry by comparison with a standard subdivided $\frac{1}{3}$ microfarad, and also to measure capacities down to ·002 microfarad against calibrated inductances, with satisfactory results when the value of Q did not exceed a few hundred ohms. When Q was 1000 ohms or over inaccuracy is likely to arise from two causes. First, self capacity of the resistances used will cause their values to depend on the frequency. In consequence, unless a pure sine-wave e.m.f. is used on the bridge, silence is not obtained

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at balance, but merely a minimum of sound which is undefined except for a change in the faint note. Second, the setting for silence is more sensitive to an error in the adjustment for D.C. balance than to an error in the adjustment for A.C. balance when Q is large. This makes it difficult to compare two minima of sound separated by the interval of time required to change to new values of S, Q, and r. It is therefore preferable to arrange that the silence is searched for by adjustments of a different nature, not interfering with the D.C. balance. Of these there are two, a continuously variable L of constant resistance and a variable condenser. In any case, values should be chosen so as to make the resistances Q and r of moderate value to minimize these two difficulties and to increase the sensitiveness of the method. The sensitiveness cannot be safely increased by increasing the voltage applied to the bridge beyond a moderate value.

When approaching a balance the conditions can be best studied by considering the origin of out-of-balance current in the telephone. In both branches of the arm the current is out of phase with the voltage V between the ends. The leading component of the current in the capacity branch is equal and opposite to the lagging component current in the inductance branch when the bridge is balanced, and the difference of these two gives rise to the note heard. The currents in the two branches in phase with V combine to give no current in the telephone at balance.

The total current in the arm is $\frac{V}{Z}$.

$$\frac{V}{Z}=V\left(\frac{1}{Q+jp\mathrm{L}}+\frac{1}{r+\frac{1}{jp\mathrm{C}}}\right)$$

$$=V\left(\frac{Q-jp\mathrm{L}}{Q^2+p^2\mathrm{L}^2}+\frac{r+j\frac{1}{p\mathrm{C}}}{r^2+\frac{1}{p^2\mathrm{C}^2}}\right).$$

The current in the arm, in quadrature with V, is

$$\mathrm{I}_1=Vp\left(\frac{\mathrm{C}}{p^2\mathrm{C}^2r^2+1}-\frac{\mathrm{L}}{Q^2+p^2\mathrm{L}^2}\right)$$

$$=Vp\left\{\frac{\mathrm{C}Q^2-\mathrm{L}+\mathrm{L}\mathrm{C}p^2(\mathrm{L}-\mathrm{C}r^2)}{(1+p^2\mathrm{C}^2r^2)(Q^2+p^2\mathrm{L}^2)}\right\}.$$

This vanishes if $\mathrm{L}=\mathrm{C}Q^2=\mathrm{C}r^2$.

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These two conditions are not equally important, as can be seen by inserting numerical values.

Let $n=830$, i. e. $p=5000$ approx.; $L=10^{-2}$ henry; $C=10^{-7}$ farad. Then $Q=r$ should be $10^{5\cdot2}$. $LCp^2=2\cdot5 \times 10^{-2}$, so that an error in $L-Cr^2$ may be 40 times as great as an error in CQ^2-L for equal effects in the telephones. The only term in the denominator of any importance is Q^2, so that on approaching balance the current which is in quadrature with V is

$$I_1=Vp\left(C-\frac{L}{Q^2}\right).$$

The component of the current in phase with V when near balance is

$$I_2=\frac{V}{Q}.$$

If Q_0 is the value of the resistance required for exact balance for both A.C. and D.C., and Q_0+dQ is the value used, the values of I_1 and ΔI_2 are

$$I_1=2Vp\frac{L}{Q_0^3}dQ,$$

$$\Delta I_2=-\frac{V}{Q_0^2}dQ,$$

and their effects in producing sound in the telephone will be proportional to these quantities. That is, they will be in the ratio

$$\frac{I_1}{\Delta I_2}=\frac{2pL}{Q_0}=2\tan\phi,$$

where ϕ is the angle of lag of the current in the inductance branch. It is therefore important for sensitiveness to keep $\frac{pL}{Q}$ large.

It follows that for ordinary values of the quantities concerned:—

1. The value of r is not critical, and may be left for final adjustment.
2. The method is not sensitive for small values of $\frac{C}{L}$, which require Q to be large.
3. The D.C. balance must be adjusted as accurately as possible if a good silence is to be obtained with A.C., *e. g.* by a slide wire in the arm S.

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Taking these points into consideration, I have found that it is not difficult to obtain results concordant to less than $\frac{1}{4}$ per cent. and in agreement with measurements made by other methods. The accuracy of the comparison is improved by the use of non-reactive resistances and by eliminating earth capacity effects.

March 5th, 1925.

XLIV. *The Passage of an Alternating Current through Sulphuric Acid.* *By* R. T. Lattey, *B.Sc., M.A., The Electrical Laboratory, Oxford**.

When an E.M.F. is applied to platinum electrodes in acid solution the products of electrolysis cause a back E.M.F., and if the applied E.M.F. be removed the electrolytic cell will discharge itself, and is, in this way, analogous to a condenser. This analogy was recognized by Varley in 1860 (1), and was more fully investigated by Kohlrausch in 1869 (2). Various attempts were made to find the "capacity" of such a condenser (1, 3, 4, 5, 6, 7) by measuring the quantity of electricity given out after a cell had been charged to a measured voltage. It was Blondlot (7) who first pointed out that, since a cell of this kind gradually loses its E.M.F. on open circuit, it is analogous to a condenser short-circuited by a fairly high resistance.

If, following Kohlrausch, we regard the back E.M.F. as being proportional to the concentration (x) of one of the products of electrolysis, then

$$v = kx; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(i.)}$$

and if the substance whose concentration is x is removed by diffusion or chemical action at a rate proportional to its concentration, then, while the cell is being charged by a current of strength i,

$$\frac{dx}{dt} = \mathrm{A}i - \mathrm{B}x, \quad \text{where A and B are constants.} \quad \text{(ii.)}$$

On open circuit we should have

$$\frac{dx}{dt} = \frac{1}{k}\frac{dv}{dt} = -\mathrm{B}x.$$

Whence $x = x_0 e^{-\mathrm{B}t}$ and $v = v_0 e^{-\mathrm{B}t}$.

According to Reichinstein (8) this law holds good, but

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his observations cannot be considered as very conclusive. It is interesting, however, to note the analogy of this law to the law $v = v_0 e^{-t/KR}$ when a condenser of capacity K is discharging through a resistance R.

Now suppose an alternating E.M F. whose value at time t is given by $v = E \sin pt$ is applied to such a cell. Combining the equation $E \sin pt = kx$ with equation (ii.), we find that when a steady state has been reached the current "leads" on the voltage by an angle ϕ whose tangent is equal to p/B. A condenser of capacity K short-circuited by a resistance R would give a current leading by $\tan^{-1} pKR$; again we see the analogy between KR and B^{-1}.

In an actual cell we have, however, the resistance of the electrolyte between the plates (r), and there is also the possibility of a resistance (S) in the surface layers of the electrodes. The complete equations then become

$$\tan \phi = \frac{pKR^2}{R + (r+S)(1+p^2K^2R^2)} \quad \text{or} \quad \frac{pkA}{(r+S)(p^2+B^2)+kAB},$$

$$\frac{E}{I} \sin \phi = \frac{pKR^2}{1+p^2K^2R^2} \quad \text{or} \quad \frac{pKA}{p^2+B^2} \qquad \text{(let us call this } 1/pC\text{)};$$

$$\frac{E}{I} \cos \phi = r + S + \frac{R}{1+p^2K^2R^2} \quad \text{or} \quad r + S + \frac{kAB}{p^2+B^2}$$

(let us call this ρ).

Statements in the literature as to the connexion between p, pC, and $\rho - r$ are very conflicting

Observer.	Reference.	Periodicity.	Law.
Oberbeck	9	480–770	$C = \text{constant}$
Gordon	10	$(30\text{–}60)10^3$	$C = \text{constant}$.
Schönherr	11	530–1700	$C = \text{constant}$.
Warburg & Strasser	12	.....	$C\sqrt{p} = \text{constant}$.
Krüger	13	390–3100	$C\sqrt{p} = \text{constant}$.
Reichinstein	14	280–640	$C\sqrt{p} = \text{constant}$.
Merritt	15	$10^4\text{–}6 \times 10^6$	$C\sqrt{p} = \text{constant}$.
Joliffe	16	$6 \times 10^5\text{–}10^7$	$C\sqrt{p} = \text{constant}$.
Sun.....	17	63–440	$C\sqrt{p} = \text{constant}$.
Wien	18	400–1600	$C = M + Np^{-1}$.
Taylor & Curtis ...	19	1500–18,000	$C = M + Np^{-1}$ and $pC(\rho - r) = \text{constant}$.
Haworth	20	620–1630	$C = M + Np^{-n}$ and $pC(\rho - r) = \text{constant}$.
Wien	21	400–1600	$pC(\rho - r) = \text{constant}$.

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Haworth's n is a fraction which approaches unity for platinized electrodes; Krüger (13) found that C was constant for electrodes which had been feebly polarized by use as cathodes with direct current but that $C\sqrt{p}$ was constant for more strongly-polarized electrodes.

Comparatively few investigators have attempted to evaluate S and R; those who have done so agree that R must be regarded as infinite (or $B=0$); while Wien (21), Haworth (20), Joliffe (16), and Taylor and Curtis (19) have found that pCS is constant.

To some extent these discrepancies may be due to the fact that with some electrodes C and S are functions of the current strength; but in many cases the applied E.M.F. was not truly sinusoidal, *e.g.* Reichinstein (14).

The majority of investigators have used comparatively high periodicities, and it seemed to be of interest to try the effect of comparatively low periodicities.

Four pairs of electrodes were used, all of which had the same dimensions—circular disks of 2 cm. radius,—and in every case the electrolyte was $H_2SO_4 . Aq.$ of maximum conductivity.

1st pair.—These were blackened by electrolysis, using a solution of chloroplatinic acid free from lead.

2nd pair.—These were first coated with platinum black by D.C. electrolysis with Lummer-Kurlbaum solution, and then heated until their surfaces were a dull mottled grey. They presumably contained a trace of lead.

3rd pair.—These were blackened like the second pair and used in a black condition.

4th pair.—These were used as received from the makers; their bright surface became dulled by use, and they acquired a dark brown surface layer which was easily removed by handling.

For the low frequencies employed a telephone was not a suitable detector when using a bridge method for measuring capacity and resistance; moreover, the only bridge method applicable to the case in hand is de Sauty's, and as this is independent of frequency, it does not afford any test of the presence or absence of harmonics in the E.M.F. wave. It was thought better to use a method which admitted the possibility of applying tests of the truly sinusoidal nature of the E.M.F. and current in the cell. Some observations were made with the well-known Joubert's wheel, and others with a rectifying commutator mounted on the same shaft as the armature of the dynamo. A commutator of this type gives average values of the current over a period corresponding to

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half a wave, and does not therefore include any terms due to even harmonics.

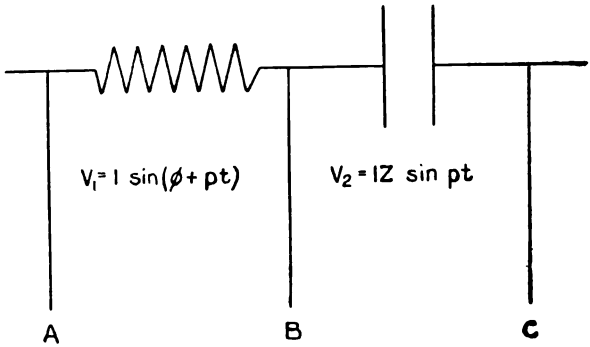
$$\frac{p}{\pi}\int_{\alpha}^{\alpha+\pi/p} \sin npt = \frac{p}{\pi}\left[-\frac{\cos npt}{np}\right] = \frac{1}{\pi n}\left[\cos\alpha - \cos(\alpha + n\pi)\right]$$

$$= \frac{2\cos\alpha}{\pi n} \text{ or } 0 \text{ according as } n \text{ is odd or even.}$$

The odd harmonics are seldom present to any appreciable extent in the voltage given by a dynamo, and hence the readings given by a rectifying commutator and galvanometer will correspond to the fundamental frequency only. Tests were made, however, and no evidence of the presence of odd harmonics could be obtained.

The position of the brushes of the commutator could be altered so that α had any desired value, and hence the complete voltage/time curve could be traced for any two points in the circuit to which they were connected. By connecting to the ends of a non-inductive 1-ohm coil (AB, fig. 1), the current/time curve could be traced. By

Fig. 1.



connecting with the terminals of the cell (BC, fig. 1) the voltage curve for this could be traced. This was done occasionally to ensure that E and I were truly sinusoidal; but the majority of the measurements were made as follows:—Galvanometer connected to AB, and commutator adjusted so that the galvanometer gave a zero reading; hence $\alpha_1 = \pi/2 = \phi + pt$; without altering the commutator, change the connexions to BC; then voltage indicated by galvanometer equals

$$\frac{2IZ}{\pi}\cos pt = \frac{2IZ}{\pi}\sin\phi = E_1.$$

Similarly, by adjusting so that the galvanometer reads zero when connected to BC and then switching over to AB, we

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have $\alpha_2 = \pi/2 = pt$ and

$$\frac{2I}{\pi}\cos(\phi + \pi/2) = -\frac{2I}{\pi}\sin\phi = -E_2.$$

Set the commutator at $(\alpha_1 - \pi/2)$, maintaining connexion to AB; the reading now corresponds to

$$\frac{2I}{\pi}\cos 0^\circ = \frac{2I}{\pi} = {}_mE_2.$$

By connecting to BC and setting the commutator at $(\alpha_2 - \pi/2)$, we get $-{}_mE_1 = \frac{2IZ}{\pi}$.

Readings were always taken for two pairs of values of α_1 and α_2 differing by 180°, so that galvanometer readings on opposite sides of the zero were obtained.

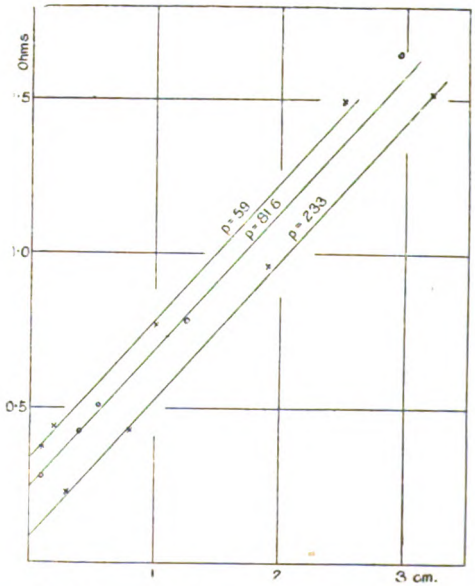
Then $\frac{E_1}{E_2} = \frac{{}_mE_1}{{}_mE_2} = Z$ and $\frac{E_1}{{}_mE_1} = \frac{E_2}{{}_mE_2} = \sin\phi$.

Hence $Z\sin\phi\,(=1/pC)$ and $Z\cos\phi\,(=\rho)$ could be calculated.

Results.

1. *Electrodes coated with pure Platinum.*—These were mounted in a tube only slightly larger in diameter than the

Fig. 2.



electrodes. In this way "edge-correction" for the resistance and capacity should be negligible. By varying the distance

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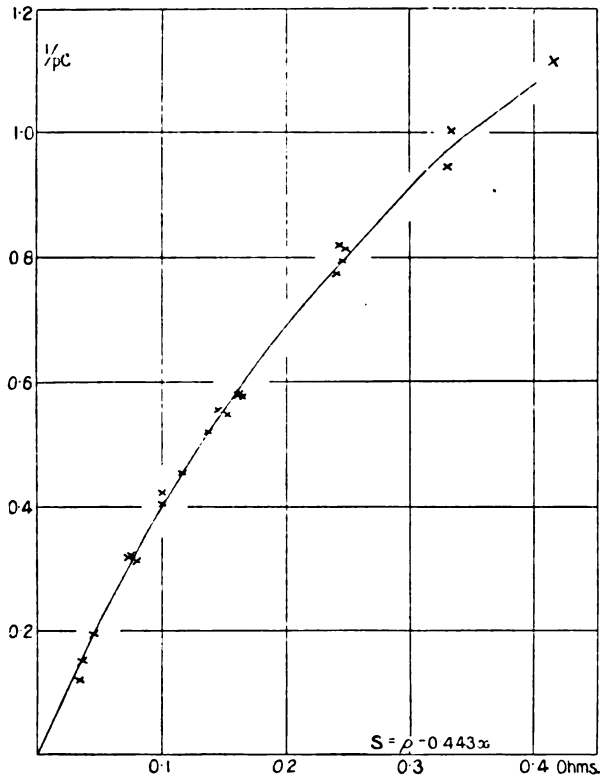
between the electrodes and keeping other factors constant, it was found that ρ was a linear function of the distance (x) between the electrodes (see fig. 2), so that we can put $\rho = kx + S$, where k is constant—in this case equal to 0·443 ohm per cm.

S is clearly a function of p such that it increases when p diminishes. In what follows, 0·443x has been subtracted from all observed values of ρ in order to obtain S.

Fig. 3.



Since it is not always easy to maintain the speed of the dynamo constant, it is better in the first instance to compare pC with S. By plotting $(pC)^{-1}$ against S (fig. 3), it is clear that a straight line does not represent the facts as it should if Wien, Haworth, or Taylor and Curtis are to be followed.

The curve drawn in fig. 3 was calculated by the equation

$$S(BpC-1) = A, \text{ where } A = 0{\cdot}51 \text{ and } B = 2{\cdot}45 \quad \text{(iii.)}$$

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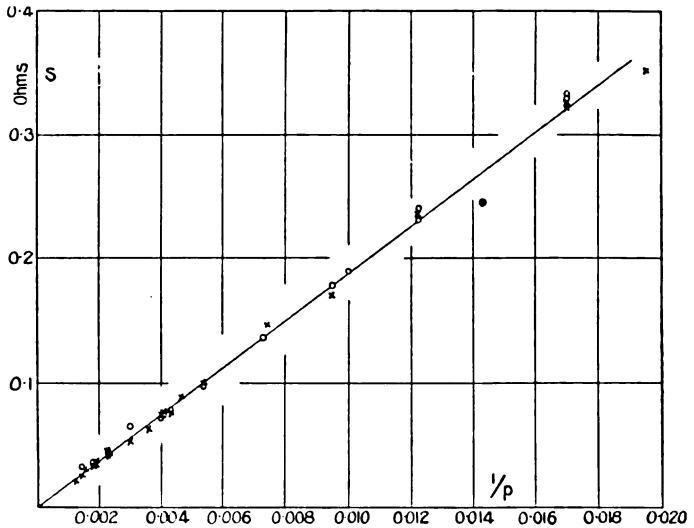
With large periodicities—*i. e.* when pC is large—this will approximate to $pCS = A/B =$ a constant, which will account for the statements of the authors quoted above, since they all used periodicities greater than 400.

In fig 4 values of S obtained directly are indicated by

Fig. 4.



circles, and those calculated from pC by the use of equation (iii.) by crosses. It will be seen that they indicate that

$$pS = D, \text{ where } D = 19{\cdot}2. \quad . \quad . \quad . \quad . \quad \text{(iv.)}$$

Combining this with equation (iii.), we have

$$pC = (pA + D)/DB = (p + 38)/92, \quad . \quad . \quad \text{(v.)}$$

which is in agreement with Wien, Taylor and Curtis, and Haworth.

2. *Grey Electrodes.*—These electrodes seemed to change their properties while an alternating current was passing, and it was very difficult to decide during a series of observations whether a steady state had been reached. The capacity seemed to depend on the strength of the current—a phenomenon observed by others in similar cases (22, 12, 23, 17, 18, 10). So far as any consistent results could be obtained, they appear to agree with a formula $308pC = p + 75 + FI$, where F is a constant and I equals current strength.

3. *Electrodes blackened with addition of Lead.*—These were set up in a large tank of acid with a distance of about 9 cm. between the electrodes. The resistance rose considerably

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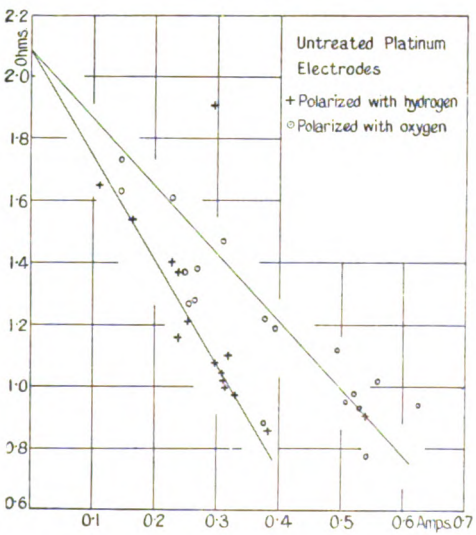
when the current was increased in strength and diminished with increase of periodicity as the following table shows :—

	I=0·14.	0·39.	0·53.
p=49·5	...	0·564	...
56·7	0·526	0·562	...
80·2	0·509	...	0·527
99·8	0·495	0·505	...
127	0·449	...	0·470
252	0·440	0·438	...
555	...	0·417	...

With currents below 0·1 amp. the effect of this factor was small compared with that of change of periodicity. But the electrodes underwent changes with time, and though, in a given series, values of ρ could be obtained which agreed with a formula $\rho = r + D/p$, the constant D changed from 7·5 to 43·5 and later to 14·25.

The capacity also changed, so that although in a given experiment $pC = A + pB$, the constants A and B changed from day to day.

Fig. 5.



4. *Untreated Electrodes.*—These gave comparatively enormous values for $(pC)^{-1}$ and for ρ, and were exceedingly erratic in behaviour. They showed one unusual feature in that the resistence fell with increase in current strength (see fig. 5). Keeping the periodicity constant at 237 and

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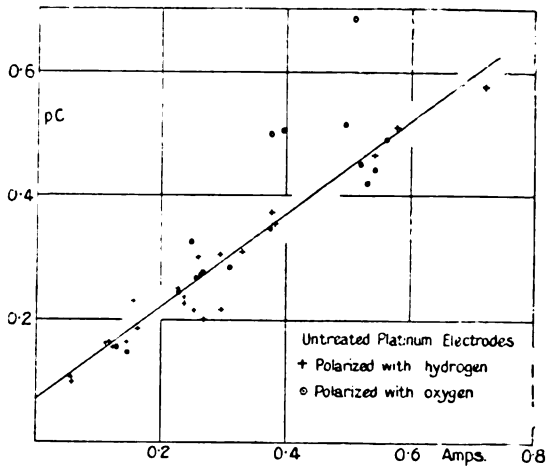
varying the current, it was clear that pC was a linear function of the current strength (see fig. 6); the experimental variations were much greater than the graph suggests, since we are here dealing with reciprocals: *e. g.*, the point

Fig. 6.



plotted as pC = 0·5 at about 0·4 amp. corresponds to an observed value of 2, whereas from the graph $(p\text{C})^{-1}$ should be $(0{\cdot}37)^{-1}$ or 2·7.

Summary.

The relationships between capacity (C), resistance (S), current strength, and periodicity (p) during the passage of an alternating current through H_2SO_4. Aq. have been investigated for values of p between 25 and 500 for four pairs of platinum electrodes.

	Effect of Increase of Current.		Effect of Increase of Periodicity.	
	(*a*) Capacity.	(*b*) Resistance.	(*a*) Capacity.	(*b*) Resistance.
1st pair ...	Negligible.	Negligible.	Decrease.	Decrease.
2nd pair ...	Increase.	*	Decrease.	*
3rd pair ...	*	Increase.	Decrease.	Decrease.
4th pair ...	Increase.	Decrease.	Decrease.	*

* Results too erratic to allow conclusions to be drawn.

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The law connecting capacity and periodicity seems to be $pC = A + pB$, and that connecting resistance with periodicity $pS = D$, where A, B, and D are constants depending on the nature and condition of the electrode surfaces.

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XLV. *On the Stress-Optical Coefficients for Direct Tension and Pressure measured in the case of Glass.* *By* S. R. SAVUR, *M.A.*, *University College, London* *.

1. *Historical.*

ONE of the fundamental assumptions made in the development of the theory of double refraction artificially produced in transparent media by mechanical stresses is that the optical effects of dilatation and compression are opposite, and that they are numerically equal when the stresses are equal. In spite of the importance of this assumption, it is

* Communicated by Prof. L. N. G. Filon, M.A., D.Sc., F.R.S.

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surprising that very few accurate experiments seem to have been made hitherto to verify it.

Brewster (1), who was the first to direct attention to the subject of artificial double refraction, did very little quantitative work on the subject. This is probably due to the fact that accurate methods of measuring double refraction were of a later origin. He was, however, the first to use the method of observing simultaneously the effects of pressure and tension by putting a rectangular beam of glass under flexure. For reasons mentioned below, it will be seen that this method is not entirely satisfactory.

Neumann (2) contented himself mainly with the mathematical development of the theory of this subject. His conclusions were adversely criticised by subsequent experimenters, notably by Kerr (3) and Pockels (4), the latter of whom pointed out serious errors of calculation in Neumann's work.

Wertheim (12) seems to have been the first to put a block of glass and other materials under pure tension and pure pressure. The magnitude of the tensions used by Wertheim was severely limited, as it was applied by cementing hangers to a glass block, and naturally could not exceed the breaking strength of the cement. He states that this tension was as high as 50 kgm. wt./cm.^{2}, but an examination of his results shows that in many cases he did not go beyond a tension of 40 bars, and that in half the number of experiments the tension did not exceed 35 bars *.

One important conclusion he deduced from his experiments is the following. The double refraction is proportional to the mechanical extension or shortening, but is not strictly proportional to the stress producing it. On plotting the double refraction or the relative retardation of the two rays against stress as abscissa, he obtained, in the case of pressure, a curve which was concave towards the axis of stress, and in the case of tension a curve which was convex towards the same axis when the stresses were small; but as the stress increased these two curves were found to approximate to a straight line which was identical in the two cases.

The next prominent name that occurs in connexion with this subject is that of Kerr (3). He also put a plate of glass under direct tension (applied by friction grips), but used only two tensions, of which the greater only amounted to

* In one isolated case, that of "Verre à glaces," his results appear to indicate that he had applied a tension as high as 80 bars (*l. c.* p. 186), but it seems difficult to admit that any cement could have withstood a tension of this magnitude.

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approximately 29 bars. On the whole, Kerr and most other experimenters have relied largely on flexure for obtaining information as regards glass under *tension*.

Two important objections may be raised against the flexure method. In the first place, in the case of a rectangular glass beam under flexure, the tension varies from point to point, and a small error in noting the position of a point on the plate will lead to a relatively large error in the calculated value of the stress-optical coefficient. A second, and more important, objection is the following. In experiments under flexure it is always presupposed that the stress varies linearly from the bottom to the top face, vanishing at the "neutral axis." This law is strictly true only in the case of perfectly elastic material; for any other material, the strain, but not necessarily the stress, follows a linear law. Moreover, if there be any permanent plastic flow, the readjustment of the material may seriously affect the stress and strain distribution, and it is known that glass shows plasticity under pressure (5).

None of the subsequent workers in this field seem to have verified this fundamental assumption, namely, that the optical effects of dilatation and compression are equal and opposite when the stresses are equal. Most of their conclusions are derived from observations of one type of stress only.

2. *Materials experimented on.*

The experiments described below were undertaken at the suggestion of Prof. Filon to test the accuracy of the law that the stress-optical coefficient is strictly the same for tension and for pressure, and particularly to see whether any deviation from the linear law, such as Wertheim suspected for small loads, actually exists. It was important to use the same specimen in both cases, as experience has shown that specimens nominally identical can differ widely in their stress-optical properties, and that even in one and the same specimen these properties can be affected by lapse of time (6). The difficulty of using the same piece of glass both for tension and for pressure lies, however, in the fact that whereas a long thin plate of glass is required for tension, a short thick one is most suitable in the case of pressure.

The plates of glass experimented upon were all supplied by Messrs. Adam Hilger & Co., with the exception of No. 1809 and U.V. 3492 originally supplied by Schott of Jena in 1906, and were of dimensions $13 \times 3 \times 1$ cm.^{3} The compositions of the glasses which are known are given in

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Table I. Only one of them (1809) showed an initial double refraction, such as would be due to a pressure parallel to the

TABLE I.

	SiO_2.	PbO.	K_2O.	Na_2O.	Al_2O_3.	CaO.	B_2O_3.	MgO.
E.D.F. 4840	30·4	64·4	1·65	1·85	0·2	1·8	—	—
H.F. 6652	41·0	51·3	3·8	1·4	0·7	0·7	—	—
1809	35·4	18·7	7·4	—	3·7	—	34·3	0·5

longest edge of the plate. The remaining four seemed free from initial double refraction : the initial relative retardation was certainly less than $0{\cdot}006\lambda$, which is the smallest retardation that could be definitely detected.

3. *Optical Arrangements.*

Parallel and plane polarized monochromatic light was passed through a uniformly stressed specimen of glass, and the relative retardation was measured with a Babinet compensator in the manner described by Filon and Jessop (7).

Three different sources of monochromatic light were used, namely, a sodium flame and the green (5461 Å.U.) and the violet (4358 Å.U.) lines of a mercury arc lamp, each of the two monochromatic radiations being isolated by means of a suitable filter. For the mercury arc a capillary mercury lamp as described by Vincent and Biggs (8) was constructed. The intensity of light from this lamp was quite sufficient, and the arc remained in action without readjustment sufficiently long to allow a large number of readings to be taken.

The light was made parallel by means of a collimator and then polarized by reflexion so that the beam was horizontal and its plane of polarization inclined at an angle of 45° to the vertical.

The compensator was of the Babinet type giving a range of relative retardation from $+\frac{3}{4}\lambda$ to $-\frac{3}{4}\lambda$ in sodium light for a linear shift of approximately 25 mm. The wedges could be moved vertically by means of a micrometer screw, and the middle of the dark band under observation was registered on a fixed cross-wire. When the violet light of the mercury arc was used it was found difficult to see the cross-wire when the band was on it, and in this case recourse was had to lateral illumination to make the wire visible.

The method of observation was as follows :—After a load

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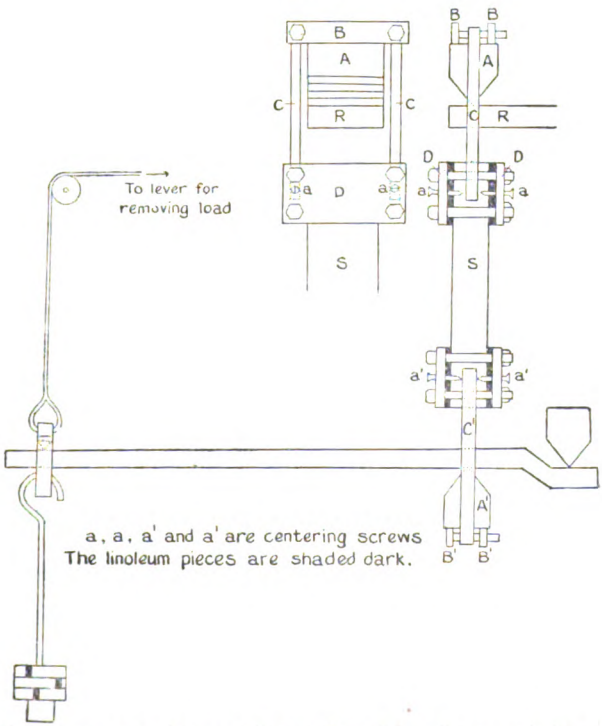
was put on, the analyser and the polarizer were crossed, and bands were seen corresponding to a relative retardation of an even number of half wave-lengths. The readings of the bands were taken, and the analyser then set parallel to the polarizer. This gave bands corresponding to a relative retardation of an odd number of half wave-lengths, giving another set of readings for the same stress and thus increasing the accuracy of the measurements. The error in a single reading was not more than about 0·013λ, and in general three readings were obtained for each load.

The optical arrangements were the same for both the pressure and the tension experiments.

4. *Apparatus for applying Direct Tension.*

The glass specimen S (fig. 1) was clamped tightly at each

Fig. 1.



end between two brass plates D with pieces of linoleum between the glass and the brass plates, so that a portion of the glass about 7 cm. long was left free in the middle. The

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plates D were suspended by an arrangement of links, shown in fig. 1, from a knife-edge block A, a similar device being used at the other end.

The tension was applied by loading a lever X Y (fig. 1), which in turn applied a downward pressure to the knife-edge A′, the knife-edge A resting on a fixed support R. In order that the plane through the knife-edges A, A′ should pass accurately through the middle of the block, centering screws a, a, a', a' were provided, giving lateral adjustment. An arrangement of levers and pulleys enabled the load to be applied or removed without jar.

As the length of the glass left free between the clamps was about seven times its thickness, it was presumed that the end effects would not reach the middle of the specimen (9), and it was found on testing with the Babinet that the tension in the middle portion of the plate could be made quite uniform for a length of approximately 3 cm., the band remaining straight and horizontal.

The pieces of linoleum were found essential to (a) improve the grip and (b) grade the shear-stress at the edges of the grip, where otherwise a concentration of stress would inevitably have caused fracture under a moderate load.

The highest tension that could be applied without slipping occurring at the grips was roughly 92 bars, corresponding to a load of about 280 kilos. The tension was varied from 92 bars to 10 bars in nine equal steps.

5. *Apparatus for applying Pressure.*

The apparatus used for producing pressure was practically the same as that described by Filon (10). The pressure was applied to the specimen by means of two knife-edge blocks pressed together by a lever, the knife-edge blocks being adjustable for centering. As the glass plates were rather long, about 13 cm., a large pressure could not be applied lest the plates should buckle. The largest pressure used was, roughly, 102 bars and was well within Euler's limit for each of the plates.

One disadvantage of using the same plate of glass for both pressure and tension was that it was not practicable to employ with safety a stress more than about 100 bars; but the maximum tension reached is considerably more than that used by previous experimenters. This gave in a few cases a relative retardation as high as two wave-lengths, while the maximum relative retardation obtained by Wertheim in

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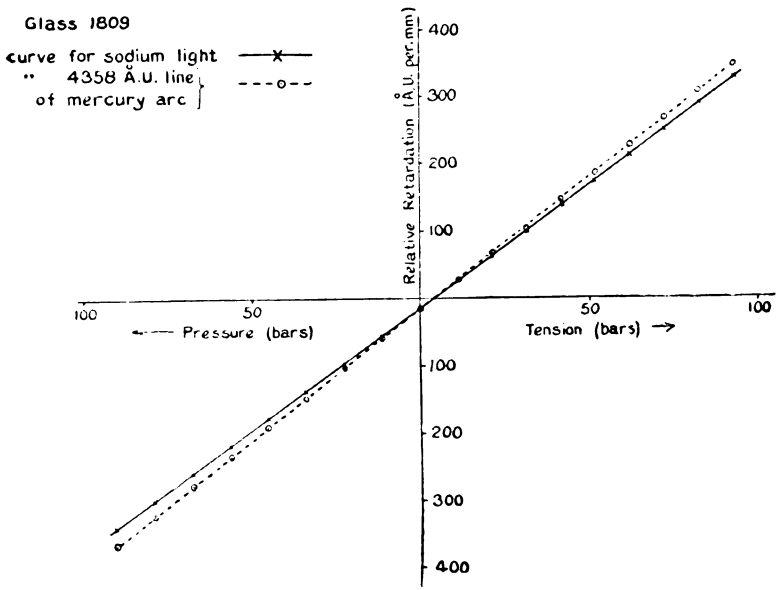
his tension experiments was, with one or two exceptions, only half a wave-length.

6. *Results obtained.*

It was observed that even under the maximum stress used the band took its final position simultaneously with the application of the load and that no residual effect could be observed when the load was completely removed, thus confirming the results (7) obtained by Filon and Jessop for glass.

The relation between the relative retardation for a given monochromatic light and the stress producing it was found to be linear in the case of the same substance, as the following diagram shows :—

Fig. 2.



The curves for the tension observations are the best fitting straight lines obtained by the method of least squares. Similar remarks apply to the pressure observations. The least square fit of a straight line for the tension and the pressure observations as a whole was also determined for each colour. It is not shown in the figure, as it would

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practically coincide with the curves already drawn. The following table gives the results more fully :—

TABLE II.

Stress-Optical Coefficient in Brewsters *.

Glass.	λ 5893 Å.U.			λ 5461 Å.U.			λ 4358 Å.U.		
	T.	P.	T+P.	T.	P.	T+P.	T.	P.	T+P.
U.V. 3492.....	3·57	3·59	3·58	3·66	3·66	3·66	3·74	3·76	3·75
E.D.F. 4840...	1·39	1·38	1·38	1·38	1·38	1·38	1·24	1·24	1·24
H.F. 6652.....	2·29	2·29	2·29	2·29	2·30	2·30	2·30	2·31	2·30
B.S.C. 7641 ...	2·69	2·72	2·70	2·71	2·74	2·73	2·80	2·82	2·81
1809	3·64	3·59	3·62	3·77	3·74	3·75	3·89	3·85	3·87

* 1 brewster = a relative retardation of 1 Å.U. per mm. per bar.

In each of the above cases the coefficient was determined from the best fitting straight line obtained from the method of least squares. T refers to tension only, P to pressure alone, and T + P to the two sets of observations taken as a whole.

It will be observed from the above table that though the individual stress-optical coefficients for tension and pressure, in the case of a given substance and monochromatic light, differ from each other by as much as 1·4 per cent. in one or two cases, yet they do not differ from the corresponding T + P coefficient by more than approximately 0·75 per cent., which is within the error estimated for the above measurements.

Fig. 3 shows the "residuals" from the straight line law in two typical cases. Two sets of residuals (calculated-observed) are shown in each diagram, the crosses indicating residuals from the best straight lines referring to tension and pressure separately, and the small circles residuals from the best straight line for both kinds of observations combined, the *sign* of the relative retardation being taken into account throughout. The upper diagram, which refers to U.V. 3592, shows the same general characteristics as the one for B.S.C. 7641, and the lower one refers to glass 1809. These two are selected as they exhibit the largest residuals.

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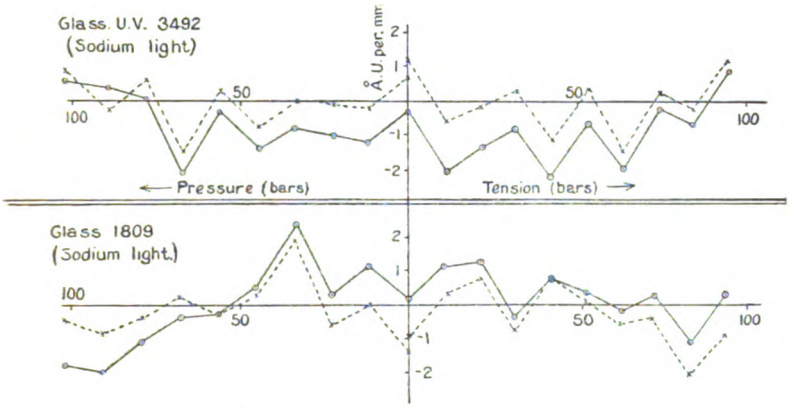
In the upper diagram the residuals shown by small circles between +50 and −50 bars are all negative, while in the lower diagram they are all positive, with one exception. This is only to be expected, for in the former case the stress-optical coefficient for tension alone is less than that for pressure alone, while in the latter the reverse is the case.

Fig. 3.



It will be noticed that very few residuals exceed 2 Å.U. per mm., which is estimated to be the greatest error of the actual measurement. Although naturally a pair of straight lines can be adjusted to give a closer fit, in every case, than a single straight line, it is very difficult to be sure that the systematic divergences indicated by fig. 3 are really significant, and they might easily be due to some systematic error, such as an error in the initial reading, which might affect all pressure readings in one sense and all tension readings in the opposite sense.

We may conclude that, within the present limits of experimental error and up to a stress of 100 bars, the law connecting double refraction and stress is accurately linear and is the same for tension and for pressure.

There is no indication of any departure from this law for small loads, as suggested by Wertheim. In his paper (*l. c.* p. 186) he states that for a borosilicate crown glass containing zinc and potash, the pressure and tension loads for a retardation of $\frac{1}{2}\lambda$ were 151 kg. and 207 kg. respectively. This very considerable difference (about 30 per cent.) is in no way borne out by the present experiments, the borosilicate

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(B.S.C. 7641) showing throughout very close agreement between the best straight lines for tension and pressure.

It seems probable that Wertheim's glass may have been imperfectly annealed: an unsuspected initial double refraction would easily account for a divergence of this kind. In the case of the present experiments, the existence of such initial double refraction was allowed for and is, in fact, indicated, where it exists, by the straight line, which fits the observations, not passing through the origin.

Nor does there appear to be any good ground for supposing that the double refraction is proportional to the strain, rather than to the stress. Wertheim's reason for suggesting this was that the general character of the strain-stress curve had certain resemblances to his retardation-stress curves. But, in view of the present observations, it seems probable that the departures of his retardation-stress curves from the linear law were due to errors of observation. The imperfect elasticity of glass is well known and, if the relation between retardation and *stress* is truly linear, it necessarily follows that the relation between retardation and strain cannot be linear.

7. *Some remarks on the Dispersion of Double Refraction in the glasses used.*

One interesting result of the experiments has been the discovery of a glass E.D.F. 4840 in which the stress-optical coefficient increases *numerically* from the violet *towards* the red.

A diagram given by Filon in 1903 (Camb. Phil. Proc. vol. xii. p. 335), showing the variation of both the stress-optical coefficient and the dispersion of double refraction in flint glass, with percentage of PbO, suggests that such a case could only occur for quite a small range of composition, between the percentage (about 66) corresponding to the vanishing of the dispersion and the percentage (about 75) corresponding to the vanishing of the stress-optical coefficient itself.

The results here obtained make $\frac{\Delta C}{\Delta \lambda}$ positive for E.D.F. 4840 (percentage of PbO, 64·4) and the dispersion sensibly nil for H.F. 6652 (percentage of PbO, 51·3). These values lie well outside the limits indicated by Filon's diagram, but it is to be noted that, whereas his dispersion is between the green and red, the dispersion here is between the indigo and yellow, so that the disagreement is probably only apparent.

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Between 5461 and 5893, E.D.F. 4840 shows practically no dispersion, which suggests far better agreement.

It would seem that the dispersion (yellow-indigo) vanishes for a much lower percentage of PbO than 66—probably more like 55. Lead glasses showing such a pronounced dispersion of abnormal type do not appear to have been examined so far. Pockels found such an effect (but not very marked) in 0·500; it was, however, exhibited strongly in a *borosilicate* glass (0·428) examined by him. There is also an isolated observation by Macé de Lépinay (11), who gives, however, no details of his glass, so that it is not known whether it was a pure flint or borosilicate.

In conclusion the author wishes to express his obligations to Prof. L. N. G. Filon and to Mr. H. T. Jessop for their valuable suggestions and criticisms during the course of this investigation, which was carried out in the Applied Mathematics and Mechanics Laboratory at University College, London.

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XLVI. *Low-Voltage Arcs in Rubidium and Cæsium Vapours.*

By F. H. Newman, *D.Sc., A.R.C.S., Professor of Physics, University College of the South-West of England, Exeter* *.

1. *Introduction.*

In a previous paper † the author has discussed the investigation of low-voltage arcs in sodium and potassium vapours, and it was shown that the potentials required to strike and maintain arcs in these vapours depend primarily

* Communicated by the Author.
† Phil. Mag. xlix. p. 1057 (1925).

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upon the vapour density and the temperature of the incandescent cathode, these potentials decreasing as the vapour density and the supply of electrons increase. The lowest striking potentials were obtained with intensely hot cathodes which, emitting a copious supply of electrons, provide conditions favourable for "photo-impact" ionization, and complete ionization of the vapour atoms is effected by electrons none of which have a velocity greater than that corresponding to the resonance potential of the vapour. In such cases the striking potential should equal the difference between the minimum ionizing and resonance potentials less the average emission energy of the electrons ejected from the cathode. Before ionization is attained the negative space charge limits the current to the value given by the well-known law $i = CE^{\frac{3}{2}}$ and also changes the uniform distribution of potential between the anode and the cathode. When this space charge is neutralized by positive ions, the arc strikes, giving a redistribution of electric intensity with a high potential fall in the immediate neighbourhood of the cathode. Under the influence of this comparatively large cathode fall an electron ionizes an atom at its first impact, and an arc can be maintained with a potential less than the ionizing potential, if the atoms are already in the metastable or partially ionized state. Before the negative space charge is annulled in this manner, some of the electrons emerge from the filament with an initial velocity which enables them to escape from the filament in spite of the negative potential gradient in the vicinity of the cathode, and the position of zero potential gradient is slightly removed from the cathode. As pointed out by Compton and Eckart * the fact that the electron current, which in low-voltage arcs is practically the entire current, flows against an opposing field is explained by the effect of diffusion arising from the large concentration gradient of the electrons. Usually this concentration gradient is negligible compared with the applied electric field, but with a high value it may become of primary importance, especially if the mean free path of the atoms is large.

These experimenters found that with abnormally low-voltage arcs in argon, operated at 6 volts, the cathode fall was invariably about 11·5 volts, which is the minimum radiating potential of argon. Under these conditions there was a reverse field of more than 5 volts existing throughout the greater part of the arc, and the electron concentration

* Phys. Rev. xxv. p. 139 (1925).

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varied from the order of 10^{12} per c.c., just outside the cathode, to about 10^{10} per c.c. near the anode. They explain this reverse field by the difference in the mobilities of the electrons and the positive ions. In their experiments the gas potential, electron energy, and electron density all increased with increasing distance from the anode towards the cathode, and the voltage actually *increased* behind the cathode, attaining the maximum value of 11 volts 3 mm. away from the incandescent filament.

It has been found that some abnormally low-voltage arcs, notably those in helium and mercury, may be explained by the existence of electrical oscillations in which the peak voltage always exceeds the lowest radiating potential of the gas. Bär, v. Laue and Meyer *, and, independently, Compton and Eckart †, have shown that these oscillations are due to current interruptions produced by the rise in the current and consequent drop in the voltage which occur when the ionization is of sufficient intensity to create a positive space charge in the neighbourhood of the filament. Under these conditions the current increases to its saturation value, and the accompanying increased potential drop in the series resistances reduces the voltage across the arc to such a value that the atoms are no longer ionized. Until the previously excited atoms resume their normal state, the current through the arc falls, and the voltage rises, as the number of atoms in the metastable condition decreases, until the excitation of the atoms commences again and the cycle is then completed. The phenomenon resembles the singing arc between carbon electrodes, except that no inductance or capacity is necessary to maintain the oscillations in the abnormally low-voltage arc.

If E_i and E_r represent the ionization and resonance potentials, respectively, and if the atoms of the vapour are in the metastable condition, it is evident that the minimum striking potential should be $E_i - E_r - E_o$, where E_o is the energy with which the electrons are emitted from the incandescent filament and depends on its temperature. Thus with rubidium vapour, the ionization and resonance potentials of which are 4·16 and 1·59 volts respectively, the minimum striking potential should be $2{\cdot}57 - E_o$ volts, and in a similar manner, $2{\cdot}43 - E_o$ volts should be the minimum striking potential with cæsium vapour.

After the arc has struck, the condition within the discharge-tube changes in two essential aspects. The

* *Zeit. f. Phys.* xx. p. 82 (1923).
† Phys. Rev. xxiv. p. 97 (1924).

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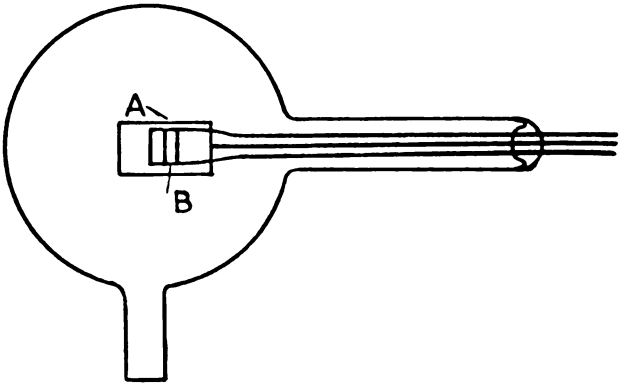
negative space charge is neutralized by the positive ions, and the electronic emission from the filament is thereby greatly increased. Saturation may be approached or reached. In addition, a cathode fall is created by the accumulation of positive ions near the cathode, and this facilitates ionization of atoms which are already in an abnormal state. It is to be expected, therefore, that the arc may be maintained with a voltage less than that required to strike the arc, and the results obtained with rubidium and cæsium vapours, described below, confirm this.

2. *Experimental Arrangement.*

The arc tube, made of glass, fig. 1, was somewhat similar

Fig. 1.



in design to that used in the previous investigations. The anode A was of sheet metal about 3 × 5 cm. in size. The incandescent cathode B consisted of three tungsten wires arranged in parallel and giving a copious supply of electrons without necessitating an unduly large potential drop between the ends. The distance between these filaments and the anode was, approximately, 3 mm. To the bottom of the discharge bulb was fused a small tube containing the metal. The whole was exhausted, and the metal then distilled, under vacuum, into the bulb. Any gases liberated during this procedure were removed by the pump and the bulb, containing a quantity of metal sufficient to form a saturated vapour at the highest temperature used, was then sealed off from the rest of the apparatus. The bulb was enclosed within an electric furnace, the temperature of which could be maintained constant within 2 or 3 degrees.

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The potential difference, obtained from a potentiometer arrangement, was regulated by a series of resistances, and was applied between the anode and the negative end of the filament, so that the voltmeter registered the maximum potential difference across the arc. In practice, the actual voltage across the filament was determined and the arcing potential difference was calculated from the centre of the filament. At low filament temperatures this method of measuring the effective voltage is probably correct, but at high temperatures it is probable that enough electrons leave the vicinity of the negative end of the filament to produce the arc, so that under these conditions the arc voltage should be measured between the anode and a point near the negative end of the filament.

3. *Experiments with Rubidium Vapour.*

With the filament current constant the striking potential was determined at different vapour pressures. The difficulty in this case was to determine the actual temperature between the electrodes since there must be a temperature gradient within the bulb owing to the heat from the filament. The latter tends to decrease the vapour density in the anode region, so that it was impossible to obtain more than an approximation of the temperature within the bulb.

It was found that above 180° C, the striking voltage and the potential necessary to maintain the arc both decreased, more or less uniformly, with increasing temperature. At each temperature the striking potential was observed several times until consecutive concordant results were obtained. One set of observations is shown in Table I. The voltages do not represent the true values; the latter being greater by the mean kinetic energy of the electrons, expressed in volts.

TABLE I.

Furnace Temperature.	Arc struck at	Arc maintained at
185° C.	7·3 volts.	7·0 volts.
200°	6·8	6·5
217°	5·9	5·5
233°	4·9	4·6
249°	4·0	3·7
265°	3·5	3·0
289°	3·2	2·3

The striking voltages with small filament currents were

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high. This fact is explained by the total bombarding electron current producing insufficient ionization to cause an arc except at electron velocities well above the critical minimum velocity. Above a certain filament temperature both the striking and maintaining potentials decreased uniformly as the current through the filament increased, but the linear relationship did not hold at low filament temperatures. At the higher temperatures the supply of electrons and their average kinetic energy both increase, especially the electron current, so that the cumulative ionization effect becomes more prominent. With the vapour at 290° C. and the filament intensely bright, the arc could be struck at 2·9 volts and maintained at 2·1 volts.

The dependence of the striking and maintaining voltages on the filament current, the discharge bulb being at 290° C., is shown in Table II.

TABLE II.

Filament Current.	Arc struck at	Arc maintained at
12·6 amps.	3·3 volts.	2·4 volts.
11·8	3·8	2·9
10·2	4·3	3·4
9·6	4·8	4·2
8·8	5·5	5·0
8·2	6·2	5·8
7·8	7·3	6·8

Table III gives the data obtained when the discharge tube was at 185° C.

TABLE III.

Filament Current.	Arc struck at	Arc maintained at
13·1 amps.	6·9 volts.	6·2 volts.
12·4	7·1	6·4
11·2	7·6	6·8
10·3	8·2	7·5
9·4	8·8	8·3
8·8	9·4	9·0
8·2	10·3	10·0

In all experiments the establishment of the arc was immediately followed by a fall in the voltage across the electrodes, this drop in potential being brought about by the neutralization of the negative space charge. The appearance of a positive space charge in the neighbourhood of the

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cathode facilitates an increased electron emission, and although the filament temperature remains constant, there will be a corresponding increase in the number of high-speed electrons emitted from the cathode. The maintenance of the arc under these conditions is due to the presence of atoms in the metastable state, the number of such atoms remaining constant. This type of ionization is important, not because of its contribution to the current, but because it facilitates the escape of additional electrons from the filament. It appears that the current through the discharge-tube must be carried in this case by the electrons, for if the positive ions were operative, their number would diminish with time and the arc would break. The electron current under these conditions is not, however, the normal electron emission which would be obtained with the heating current and applied voltage, since the positive space charge increases this normal electron current.

With rubidium vapour the chief factors which determine the production of low-voltage arcs are the high vapour density and the copious supply of electrons emitted from the incandescent cathode. Photo-impact ionization is, probably, particularly active in this case and accounts for the arc striking at potentials well below the ionization potential—4·16 volts—demanded by the quantum theory.

4. *Experiments with Cæsium Vapour.*

A discharge-tube similar to that shown in fig. 1 was used for the experiments with cæsium vapour, and the results obtained resembled those given by rubidium. In all cases ionization was observed below the ionization potential when the vapour density and electron densities were high. Under these conditions more electron-atomic collisions occur, more radiation is emitted and more is absorbed. The ionization and resonance potentials of cæsium vapour are 3·88 and 1·45 volts respectively, so that it should be possible, therefore, to strike the arc with an applied potential of $2{\cdot}43 - E_0$ volts, where E_0 represents the kinetic energy of the emitted electrons.

With the tungsten filament intensely bright and the vapour at 285° C., the arc could be struck readily at 2·6 volts and maintained at 1·9 volts. As the temperature of the discharge bulb was lowered these voltages increased in the way shown in Table IV. This is to be expected since a lower vapour density means fewer electron-atomic collisions and less radiation emitted.

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TABLE IV.

Temperature of Furnace.	Arc struck at	Arc maintained at
164° C.	6·9 volts.	6·5 volts.
183°	5·8	5·4
201°	5·2	4·6
234°	4·1	3·4
252°	3·7	2·9
276°	3·1	2·3
295°	2·8	2·0

Table V. gives the striking and maintenance potentials with different filament currents, the temperature of the electric heater being 281° C.

TABLE V.

Filament Current.	Arc struck at	Arc maintained at
13·9 amps.	2·7 volts.	2·0 volts.
12·6	3·4	2·5
11·9	4·0	2·9
10·9	5·0	3·9
10·2	5·9	5·0
9·3	7·3	6·6
8·5	8·9	8·6

5. *Conclusions.*

It is evident that in cases where cumulative ionization is predominant low-voltage arcs may be maintained in vapours at voltages considerably lower than their ionization potentials. Atoms in the metastable condition are then ionized by direct impact, and the negative space charge around the incandescent filament is neutralized. As a result the supply of electrons is no longer entirely decided by the temperature of the filament, but there is in the immediate neighbourhood of the cathode an accelerating field which increases the electron current to its saturation value. It is possible to strike and maintain arcs in rubidium and cæsium vapours at potentials less than the ionization potential when the vapour density is high and when there is an intense electronic emission from the incandescent cathode.

XLVII. *A proposed Model for the Alpha Particle, and some Nuclear Series.* By R. HARGREAVES *.

§ 1. THE present attempt to deal with some nuclear structures has a fundamental principle in common with an earlier paper † on Atomic Systems, but there is a substantial difference in the way the principle is applied. The principle is that atom or nucleus consists

* Communicated by the Author.
† Phil. Mag. December 1922.

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of separate unit electrons—positive and negative. The paper combined these in one neutral structure; here they are separated into two groups, and we are now concerned with the inner group or nucleus.

Aston's theory of isotopes, in conjunction with the theory of spectral lines, suggests the assumptions which are made the basis of these structures.

(*a*) The atomic *weight* p, as narrowed by the use of a single isotope, is the number of positive electrons contained in the nucleus.

(*b*) The atomic *number* q is the number of negative electrons moving as satellites in orbits external to the nucleus, and controlled by the positive residue of the nucleus.

The difference $p-q$ is the number of negative electrons engaged in binding together the positive units so as to form a structure. The nucleus is taken to be a structure in the sense that all units contained revolve about a common axis, with their relative positions unaltered, under attractions and repulsions following electrostatic law. Further, it is supposed that nuclear orbits are on a much smaller scale than those of satellites.

It will follow that for the moderate range of the atomic number for which calculations are given, the reaction of satellites on elements of the nucleus will be small in comparison with the mutual action of the latter. It then becomes admissible to consider the nucleus independently of the external satellites: with large atomic numbers the assumption might be precarious.

Though an opinion that the nucleus is composite may be generally entertained, it is a somewhat hazardous adventure to put forward a definite structural scheme, even for a limited range of atomic numbers. The difficulties in making a structure conform to the requirements of atomic weights and numbers are serious enough, as the present attempt will illustrate. If these are overcome, there is I think an eventual test by reference to the spectral influences of the composite nucleus, the nature of which may be indicated. A composite nucleus gives a force only approximately that due to its positive residue acting at the centre. The departure from a normal potential energy has an effect on the orbits of satellites resembling that disclosed by Sommerfeld's treatment of a variable inertia, an effect due in each case to a second period involved. A comparison with observed spectra must

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constitute a check on any proposed arrangement of the electrons within the nucleus.

§ 2. The scheme had its origin in the discovery of what seemed a reasonable model for the α particle. It differs from a model proposed by Lenz, and has the distinctive feature that the type can be extended into a series.

Now processes of disintegration natural or artificial point to a certain dominance of the helium type, which may be interpreted in two ways. It may be taken as demanding the assumption of a third fundamental entity in addition to the single positive and negative units, or as suggesting that the structure characteristic of the helium nucleus is one which admits of extension.

Further, the range of smaller atomic numbers comprises cases in which $p=2q$ as for helium, and others for which $p-2q=1$, the former suggesting a continuation of the type, the latter making a new call.

I now describe the primary series,—a triplane model.

In the upper and lower of three parallel equidistant planes equal circles are described by positive electrons, in the middle plane a circle of smaller radius is described by negative electrons, all circles having their centres on a common axis perpendicular to the planes. Each circle contains n elements equally spaced; positive lies over positive, but negative elements are in azimuth halfway between the positive. The circles are described with a common angular velocity.

Thus, for example, in the α model the four positive electrons lie at any moment at the four corners of a rectangle, the two negative at the ends of a perpendicular to the rectangle drawn through its middle point. The axis of rotation is a line through the middle of the rectangle drawn parallel to its shorter sides.

Attention may be called to two features of the model:—the position of the negative electrons in a plane between the planes of the positives, and on a circle of smaller radius, is one which gives strong protection to the more mobile electrons; the heavy positive electrons are placed where they contribute best to angular momentum.

§ 3. In virtue of the symmetry the dynamical equations are reduced to three, one securing the absence of an axial component of force on the positive elements, and two giving inertial forces in terms of attractions and repulsions for positive and for negative electrons. For helium ($n=2$) the inertial force on a negative electron has a less ratio than 1 : 3000 to that on a positive, and for higher values of n at any rate the ratio is less than 1 : 1840. If we are content with an accuracy of 1 in 1000, the inertial

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force on a negative element may be neglected, that is such element must be very close to a position of equilibrium. We can then regard two of the equations as equations of condition determining the ratios of three distances, two radii and the perpendicular distance between planes; while the third gives the velocity of rotation.

Numerical solutions have been found for this primary series (i.) in the cases $n=2$, 3, and 4. In the two latter the solution is by trial, and the labour of course increases with the increasing number of attractions and repulsions. I have found it possible to obtain asymptotic formulæ for the sums of attractive and repulsive forces, based on the cosecant series considered in the former paper. The method gives simple results so long as only the terms of highest order are used, but the greater complexity of the present problem makes it laborious to deal with terms of less order.

It appears that the two equations described above as equations of condition can always be satisfied; but the third equation, which gives the value of ω^2 (ω=angular velocity), makes that value positive up to a certain value of n and thereafter negative. With only terms of highest order the value $n=18$ is indicated as final, but some examination of terms of lower order suggests an extension to $n=20$.

§ 4. Other series have been examined in which an addition is made to the primary form.

In series (ii.) the addition is that of a negative electron at the centre of the system. Solutions are found for $n=2$ and 3, main terms in the asymptotic value make ω^2 vanish for n between 23 and 24, and with terms of lower order $n=24$ is probably included.

In connexion with this series a new feature arises, viz. the question of stability of the central electron in respect to axial displacement. The position is unstable for small values of n, stable for higher values, with a place of transition only approximately determined (*cf.* § 7).

Where the series is applicable there are $2n$ positive and $n+1$ negative electrons within the nucleus, $(n-1)$ satellites; or if we call these $2q+2$, $q+2$, q, then $p=2q+2$. Thus with $n=23$ and 24 for the last two, these have $q=22$ and 23, $p=46$ and 48.

In series (iii.) the addition is that of two negative electrons on the axis at equal distances from the centre. A new variable is introduced with a corresponding condition for the equilibrium of the axial electrons, which greatly adds to the labour of numerical solution; and in fact only one has been found for the opening case $n=3$. The main term in the value of ω^2 is found to vanish for a value of n between 26

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and 27, and the latter value is probably included when terms of lower order are taken into account.

The nucleus has $2n$ positive and $n+2$ negative electrons, and the number of satellites is $n-2$; or if these numbers are $2q+4$, $q+4$, q, then $p=2q+4$. The series opens with $q=1$, $p=6$, an isotope of hydrogen with mass 6; the last two have $n=26$, 27 or $q=24$, 25 and $p=52$, 54, and an intermediate case $n=20$ has $q=18$, $p=40$.

A modification of series (iii.) by the further addition of a positive electron at the centre has been examined and a numerical solution found for $n=3$. A difficulty arises in the application of the asymptotic method which I have interpreted as implying a very restricted series. The opening term with $n=3$, $q=2$, $p=7$ corresponds to an isotope of helium.

§ 5. It will be observed that the series (i.) terminates through lack of attracting power on the positive rings, a fact which points to the need for negative electrons in a higher ratio than 1 : 2 to the positive within the nucleus, to make a structure.

The only type which yields an odd number for isotope is the modified form of (iii.), a short series. In respect to odd values of atomic weights obtained otherwise than by a mixture of even isotopes, three types of addition to the primary series (i.) may be mentioned:—

(*a*) a pair near the centre,

(*b*) a central positive electron with two negatives revolving round it,

and (*c*) a central positive electron with three negatives revolving round it.

These additions give atomic weights and numbers corresponding to those in the series (i.), (ii.), and (iii.), but with a unit added to the weight. The configurations differ from the series types by always showing some departure from symmetry, and so there is left a problem of coordinating the added elements with the primary structure, which I have not faced.

A suggestion for dealing with higher atomic numbers will be made later, in which the proportion of negative to positive elements within the nucleus is gradually increased as the atomic number increases, where also odd and even isotopes stand on the same footing. *Cf.* § 16.

Numerical Solutions.

§ 6. It is proposed to write in detail the solution for the α particle, and to give a brief note of other numerical solutions. Take the radius of the circle described by the

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negative electron as 1, that described by the positive electrons as a, and let $2b$ be the distance between the extreme planes. The three equations are then

$$\frac{1}{4}=\frac{4}{(1+a^2+b^2)^{3/2}},\quad \frac{1}{4b^2}+\frac{2b}{(4a^2+4b^2)^{3/2}}=\frac{2b}{(1+a^2+b^2)^{3/2}},$$

$$m_1\omega^2 a/\epsilon^2=-\frac{1}{4a^2}-\frac{2a}{(4a^2+4b^2)^{3/2}}+\frac{2a}{(1+a^2+b^2)^{3/2}}, \quad . \quad . \quad (1)$$

where in the first equation $m_2\omega^2/\epsilon^2$ is omitted, since m_2 and m_1 being masses of negative and positive electrons $m_2:m_1 a$ is less than 1 : 3000. The first equation yields $a^2+b^2=5{\cdot}3496$, the second is then $\frac{1}{b^3}=\frac{1}{2}-\frac{1}{(5{\cdot}3496)^{3/2}}={\cdot}41918$, and so $b=1{\cdot}3362$, $b^2=1{\cdot}7854$, $a^2=3{\cdot}5642$, $a=1{\cdot}8879$. The third equation gives $m_1\omega^2 a={\cdot}12795\epsilon^2$.

The kinetic energy is $(2m_1a^2+m_2)\omega^2$, and it is sufficient to write $K=2m_1a^2\omega^2$; the angular momentum is $(4m_1a^2+2m_2)\omega$, and it is sufficient to write $A=4m_1a^2\omega$.

In writing (1) and similar equations it is convenient to use ratios, but it is desirable to express the results in terms of r_1 the radius of the circle described by positive electrons. To pass from $m_1\omega^2 a={\cdot}12795\epsilon^2$, both sides are multiplied by a^2, then r_1 is written for a on the left hand and the numerical value of a^2 on the right hand. The solution may then be stated in the form

$$m_1\omega^2 r_1^3={\cdot}4560\epsilon^2,\quad K={\cdot}9121\epsilon^2/r_1,\quad A=4\epsilon\sqrt{m_1r_1}\times{\cdot}6753,$$
$$KA^2=4^2\epsilon^4 m_1\times{\cdot}4195. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

For $n=3$ the equations are :

$$\left.\begin{aligned}
&\frac{1}{\sqrt{3}}=\frac{2(2-a)}{(a^2-a+1+b^2)^{3/2}}+\frac{2(1+a)}{(1+a^2+b^2)^{3/2}},\\
&\frac{2b}{(a^2-a+1+b^2)^{3/2}}+\frac{b}{(a+1^2+b^2)^{3/2}}=\frac{1}{4b^2}+\frac{4b}{(3a^2+4b^2)^{3/2}},\\
&\text{and}\\
&m_1\omega^2 a/\epsilon^2=-\frac{1}{a^2\sqrt{3}}-\frac{3a}{(3a^2+4b^2)^{3/2}}+\frac{1+a}{(1+a^2+b^2)^{3/2}}\\
&\qquad\qquad+\frac{2a-1}{(a^2-a+1+b^2)^{3/2}}.\\
&\text{The solution is}\quad a=1{\cdot}4684,\ b={\cdot}8112,\ m_1\omega^2 a={\cdot}25157,\\
&\text{and as referred to } r_1\\
&m_1\omega^2 r_1^3={\cdot}5752\epsilon^2,\quad K=1{\cdot}6273\epsilon^2/r_1,\\
&A=6\epsilon^2\sqrt{m_1r_1}\times{\cdot}7365,\quad KA^2=6^2\epsilon^4 m_1\times{\cdot}8827.
\end{aligned}\right\}\ (3)$$

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For $n=4$, the solution is

$$a=1{\cdot}3013,\quad b={\cdot}5859,\quad m_1\omega^2 a={\cdot}3397,$$

and as referred to r_1

$$m_1\omega^2 r_1^3={\cdot}5752\epsilon^2,\qquad \mathrm{K}=2{\cdot}301\epsilon^2/r_1,$$

$$\mathrm{A}=8\epsilon^2\sqrt{m_1 r_1}\times{\cdot}7584,\quad \mathrm{KA}^2=8^2\epsilon^4 m_1\times 1{\cdot}3235. \qquad (4)$$

§ 7. Though the opening cases in series (ii.) are considered unstable, it may be well to state the solutions. For $n=2$ the equations (1) are modified to

$$1+\frac{1}{4}=\frac{4}{(1+a^2+b^2)^{3/2}},$$

$$\frac{1}{4b^2}+\frac{2b}{(4a^2+4b^2)^{3/2}}=\frac{2b}{(1+a^2+b^2)^{3/2}}+\frac{b}{(a^2+b^2)^{3/2}},$$

and

$$m_1\omega^2 a=\frac{a}{(a^2+b^2)^{3/2}}+\frac{2a}{(1+a^2+b^2)^{3/2}}-\frac{1}{4a^2}-\frac{2a}{(4a^2+4b^2)^{3/2}}; \qquad (5)$$

with a solution

$$a={\cdot}9072,\quad b={\cdot}5901,\quad m_1\omega^2\alpha={\cdot}8002\epsilon^2;$$

leading to

$$m_1\omega^2 r_1^3={\cdot}6585\epsilon^2.$$

For $n=3$, the solution is

$$a=1{\cdot}069,\quad b={\cdot}5481,\quad m_1\omega^2 a={\cdot}7603\epsilon^2;$$

leading to

$$m_1\omega^2 r_1^3={\cdot}8072\epsilon^2. \qquad (6)$$

The position as regards the axial stability of the central electron turns on the sign of the coefficient of z^2 in the expansion of

$$(1+z^2)^{-\frac{1}{2}}-(a^2+\overline{b-z}^2)^{-\frac{3}{2}}-(a^2+\overline{b+z}^2)^{-\frac{3}{2}},$$

where z is a small axial displacement of the electron. This coefficient is $-\frac{1}{2}+\frac{a^2-2b^2}{(a^2+b^2)^{5/2}}$; the first term only, due to the circle of negative electrons, would give instability, and accordingly stability demands a condition

$$2a^2-4b^2>(a^2+b^2)^{5/2}. \qquad (7)$$

If we write the sign of equality, and then differentiate with regard to a^2 to get a further equation $4=5(a^2+b^2)^{3/2}$, the combination gives values $a^2={\cdot}6894$, $b^2={\cdot}1723$. The position is then that no case of the inequality occurs if $b^2>{\cdot}1723$; but as b^2 is diminished there is a range of values

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of a^2 above and below ·6894 for which the condition is satisfied, and this range is continually extended until when b approaches 0, the range of a is from 0 to $\sqrt[3]{2}$ or 1·26. Judging from the values of a, I estimate that the inequality first holds for $n=8$, which corresponds to $q=7$.

This discussion of stability has an application to the addition of a pair to the primary series suggested above (*cf.* § 5). For the opening terms the position, being unstable for a negative electron at the centre, is stable for a positive electron. The pair would therefore have its positive element very close to the centre, and a dynamical complication which would attach to the reverse arrangement is minimized. This addition of a pair would in the case of $n=3$ make $p=7$, $q=3$ an isotope of lithium.

§ 8. For type (iii.) a single case $n=3$ has been solved. With $+c$ and $-c$ for the axial positions of the added negative electrons, the equations are:

$$\left.\begin{aligned}
&\frac{1}{\sqrt{3}}+\frac{2}{(1+c^2)^{3/2}}=\frac{2(2-a)}{(a^2-a+1+b^2)^{3/2}}+\frac{2(1+a)}{(a+1)^2+b^2)^{3/2}},\\
&\frac{2b}{(a^2-a+1+b^2)^{3/2}}+\frac{b}{(a+1)^2+b^2)^{3/2}}+\frac{b-c}{(a^2+b-c)^2)^{3/2}}\\
&\qquad+\frac{b+c}{(a^2+b+c)^2)^{3/2}}=\frac{1}{4b^2}+\frac{4b}{(3a^2+4b^2)^{3/2}},\\
&\frac{3(b+c)}{(a^2+b+c)^2)^{3/2}}=\frac{3(b-c)}{(a^2+b-c)^2)^{3/2}}+\frac{3c}{(1+c^2)^{3/2}}+\frac{1}{4c^2},\\
&m_1\omega^2a/\epsilon^2=-\frac{1}{a^2\sqrt{3}}-\frac{3a}{(3a^2+4b^2)^{3/2}}+\frac{1+a}{(1+a)^2+b^2)^{3/2}}\\
&\qquad+\frac{2a-1}{(a^2-a+1+b^2)^{3/2}}+\frac{a}{(a^2+b+c)^2)^{3/2}}+\frac{a}{(a^2+b-c)^2)^{3/2}};\\
&\text{of which the solution gives}\\
&\qquad a=1{\cdot}126,\ b={\cdot}707,\ c=1{\cdot}075,\ m_1\omega^2a={\cdot}8844\epsilon^2,\\
&\text{leading to}\\
&\qquad m_1\omega^2r_1^3=1{\cdot}121\epsilon^2.
\end{aligned}\right\}\quad(8)$$

When the equations are modified to correspond with the addition of a positive electron at the centre, the solution obtained is:

$$\left.\begin{aligned}
&a=1{\cdot}803,\ b={\cdot}987,\ c=1{\cdot}008,\ m_1\omega^2a/\epsilon^2={\cdot}4245;\\
&\text{leading to}\\
&\qquad m_1\omega^2r_1^3=1{\cdot}381\epsilon^2.
\end{aligned}\right\}\quad(9)$$

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§ 9. Application of Quantum.—The numerical solutions give the ratios of the three distances concerned in (i.) and (ii.), and of the four concerned in (iii.). The scale on which the system is constructed is so far arbitrary. After some hesitation I have set down values in which the system is made definite by equating the angular momentum of each positive electron to the standard angular momentum $h/2\pi$ of Planck's method. The combination of equations

$$m_1\omega r_1^2 = h/2\pi \quad \text{and} \quad m_1\omega^2 r_1^3 = \mathrm{N}\epsilon^2 \quad . \quad . \quad (10)$$

will then be found to yield the following results :—

$$r_1 = 2{\cdot}89\times10^{-12}\times\mathrm{N}^{-1}, \quad \mathrm{K} = m_1\mathrm{V}^2\times5{\cdot}29\times10^{-5}\times n\mathrm{N}^2,$$
$$v/\mathrm{V} = 7{\cdot}27\times10^{-3}\times\mathrm{N}\,; \quad . \quad . \quad . \quad . \quad (11)$$

where v/V is the ratio of linear velocity of a positive electron to that of light.

These numbers are based on the values of constants given by

$$h = 6{\cdot}565\times10^{-27}, \quad \epsilon = 4{\cdot}774\times10^{-10}, \quad \epsilon/m_2 = 5{\cdot}3\times10^{17},$$
$$m_1/m_2 = 1840. \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

A table of some numerical values will be given when the asymptotic position has been dealt with. *Cf.* § 14.

§ 10. Asymptotic Values.—The general form of the equations for the primary series will be set down with a view to considering asymptotic values* when n is great. The fact that the inertial force on a negative electron is negligible is expressed by the equation

$$\frac{c_n}{2} = \sum_{r=0}^{r=n-1} \frac{2(1-a\cos\theta_r)}{(1+a^2+b^2-2a\cos\theta_r)^{3/2}}\,; \quad . \quad . \quad . \quad (\mathrm{A})$$

in which $\theta_r = (2r+1)\pi/n$, and c_n defined as $\frac{1}{2}\sum_{s=1}^{s=n-1}\operatorname{cosec} s\pi/n$ has the asymptotic value

$$c_n = \frac{n}{\pi}\left(\log_e n + \gamma - \log_e\frac{\pi}{2}\right). \quad (13)$$

The vanishing of the axial component of force on a positive electron is secured by an equation

$$\sum_{r=0}^{r=n-1} \frac{b}{(1+a^2+b^2-2a\cos\theta_r)^{3/2}}$$
$$= \frac{1}{4b^2} + \sum_{s=1}^{s=n-1} \frac{2b}{(2a^2+4b^2-2a^2\cos\theta_s)^{3/2}}, \quad . \quad (\mathrm{B})$$

in which $\theta_s = 2s\pi/n$.

* For the analysis *cf. op. cit.*, section Mathematical Theory.

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A third equation gives the value of ω^2, viz.

$$m_1\omega^2 a/\epsilon^2 = -\frac{c_n}{2a^2} - \sum_{s=1}^{s=n-1} \frac{a(1-\cos\theta_s)}{(2a^2+4b^2-2a^2\cos\theta_s)^{3/2}}$$
$$+ \sum_{r=0}^{r=n-1} \frac{a-\cos\theta_r}{(1+a^2+b^2-2a\cos\theta_r)^{3/2}}. \quad (13)$$

To deal with asymptotic values we require at the outset some conception of the probable order of the quantities. In the double ring of earlier work, x being a ratio of radii of circles in one plane, I found $(x-1)n^2$ to be a finite quantity, and with this in mind looked to some modification of the type $\alpha+\beta\log n$ for $(a-1)n^2$. The forecast is verified and permits a reduction of $1+a^2+b^2-2a\cos\theta_r$ to a form $b^2+2a(1-\cos\theta_r)$ or $b^2+4a\sin^2\theta_r/2$, and $2a^2+4b^2-2a^2\cos\theta_s$ to a form $4(b^2+a^2\sin^2\theta_s/2)$.

Further to make use of the binomial expansion we need some assurance of the relative values of b and $\sin\theta_r/2$. For this purpose a limiting case may be considered in which an infinite lattice-work is taken as model. In each of two infinite parallel lines positive units are placed at distance $2x$, positive opposite to positive, so that four adjacent units form a rectangle of sides $2x, 2y$. Negative units are placed at the centre of each rectangle. The condition of equilibrium in its original form is

$$\frac{1}{4y^2} + \frac{4y}{(4x^2+4y^2)^{3/2}} + \frac{4y}{(16x^2+4y^2)^{3/2}} + \frac{4y}{(36x^2+4y^2)^{3/2}} + \dots$$
$$= \frac{2y}{(x^2+y^2)^{3/2}} + \frac{2y}{(9x^2+y^2)^{3/2}} + \frac{2y}{(25x^2+y^2)^{3/2}} + \dots,$$

or

$$\frac{1}{8y^3} + \frac{1}{4(x^2+y^2)^{3/2}} + \frac{1}{4(4x^2+y^2)^{3/2}} + \frac{1}{4(9x^2+y^2)^{3/2}} + \dots$$
$$= \frac{1}{(x^2+y^2)^{3/2}} + \frac{1}{(9x^2+y^2)^{3/2}} + \frac{1}{(25x^2+y^2)^{3/2}} + \dots,$$

or with $y^2=\mu x^2$,

$$\frac{1}{2\mu^{3/2}} + \frac{1}{(2^2+\mu)^{3/2}} + \frac{1}{(4^2+\mu)^{3/2}} + \frac{1}{(6^2+\mu)^{3/2}} + \dots$$
$$= 3\left[\frac{1}{(1+\mu)^{3/2}} + \frac{1}{(3^2+\mu)^{3/2}} + \frac{1}{(5^2+\mu)^{3/2}} + \dots\right]. \quad (14)$$

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If $\mu<1$ expansion of each term by the binomial may be made, and with a notation

$$S_3=\frac{1}{1^3}+\frac{1}{2^3}+\frac{1}{3^3}+\ldots,\quad T_3=\frac{1}{1^3}+\frac{1}{3^3}+\frac{1}{5^3}+\ldots,$$

and use of the property $S_3/2^3=S_3-T_3$, the equation takes the form

$$\frac{1}{2\mu^{3/2}}+S_3-\frac{3}{2}\mu S_5+\frac{3.5}{2.4}\mu^2 S_7-\ldots$$
$$=4\left(T_3-\frac{3}{2}\mu T_5+\frac{3.5}{2.4}\mu^2 T_7-\ldots\right). \quad . \quad . \quad (15)$$

The solution $\mu=\cdot 4308$ (*v. infra*) justifies the expansion, and in the circular problem where x is replaced by $a\pi/n$, we shall find that br proves finite, and b is less than the least value of $2\sin\theta_r/2$ or $2\sin\pi/2n$. Accordingly we may write

$$(1+a^2+b^2-2a\cos\theta_r)^{-3/2}$$
$$=\{2a(1-\cos\theta_r)+b^2\}^{-3/2}$$
$$=\frac{\operatorname{cosec}^3\theta_r/2}{8a^{3/2}}\left[1-\frac{3}{2}\cdot\frac{b^2}{2^2a}\operatorname{cosec}^2\theta_r/2\right.$$
$$\left.+\frac{3.5}{2.4}\frac{b^4}{2^4a^2}\operatorname{cosec}^4\theta_r/2-\ldots\right],$$

or with Σ_3 for $\sum\limits_{r=0}^{r=n-1}\operatorname{cosec}^3\theta_r/2$,

$$\sum_{r=0}^{r=n-1}(1+a^2+b^2-2a\cos\theta_r)^{-3/2}$$
$$=\frac{1}{8a^{3/2}}\left(\Sigma_3-\frac{3}{2}\cdot\frac{b^2}{2^2a}\Sigma_5+\frac{3.5}{2.4}\frac{b^4}{2^4a^2}\Sigma_7\right). \quad . \quad (16)$$

If we write main terms only,

$$\Sigma_3=2T_3\times\left(\frac{2n}{\pi}\right)^3,\ \Sigma_5=2T_5\times\left(\frac{2n}{\pi}\right)^5, \quad . \quad . \quad . \quad (17)$$

and then the main term in $\sum\limits_{r=0}^{r=n-1}(1+a^2+b^2-2a\cos\theta_r)^{-3/2}$ is

$$\frac{2n^3}{\pi^3a^{3/2}}\left(T_3-\frac{3}{2}\beta T_5+\frac{3.5}{2.4}\beta^2T_7\ldots\right), \quad . \quad . \quad . \quad (18)$$

where β is used for $b^2n^2/a\pi^2$.

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To deal with $\{2a^2(1-\cos\theta_s)+b^2\}^{-3/2}$ we need a formula $2S_3\times\left(\frac{n}{\pi}\right)^3$ for the main term of

$$\sum_{s=1}^{s=n-1}\operatorname{cosec}^3 s\pi/n, \quad . \quad . \quad . \quad . \quad . \quad (19)$$

and so obtain as main term of $\sum_{s=1}^{s=n-1}(2a^2+4b^2-2a^2\cos\theta_s)^{-3/2}$ the value

$$\frac{n^3}{4\pi^3a^3}\left(S_3-\frac{3}{2}\frac{\beta}{a}S_5+\frac{3\,.\,5}{2\,.\,4}\frac{\beta^2}{a^2}S_7\ldots\right). \quad . \quad . \quad . \quad (20)$$

The condition (B) is therefore expressed by

$$2(T_3-\tfrac{3}{2}\beta T_5+\ldots)=\frac{1}{4\beta^{3/2}}+\frac{1}{2a^{3/2}}\left(S_3-\frac{3}{2}\frac{\beta}{a}S_5+\ldots\right). \quad (21)$$

The asymptotic form in which a is written $=1$ is

$$2(T_3-\tfrac{3}{2}\beta T_5+\ldots)=\frac{1}{4\beta^{3/2}}+\tfrac{1}{2}(S_3-\tfrac{3}{2}\beta S_5+\ldots); \quad . \quad (22)$$

it agrees with (15) above, and depends not only on the use of $a=1$ but also on accepting as sufficient the main terms in the values of Σ_3....

§ 11. In dealing with (A) the numerator $1-a\cos\theta_r$ is written as $a(1-\cos\theta_r)-(a-1)$, and so long as only a main term is in question we treat a as 1 in the various expansions. In the series with $1-\cos\theta_r$ as numerator we have Σ_1 appearing which is $2(c_{2n}-c_n)$, and then (A) is represented by

$$\frac{c_n}{4}=\tfrac{1}{2}(c_{2n}-c_n)-\frac{n}{\pi}\left(\frac{3}{2}\beta T_3-\frac{3\,.\,5}{2\,.\,4}\beta^2T_5+\ldots\right)$$
$$-\frac{2n^3(a-1)}{\pi^3}(T_3-\tfrac{3}{2}\beta T_5+\ldots),$$

or by

$$\frac{2n^2(a-1)}{\pi^2}\left(T_3-\frac{3\beta}{2}T_5+\ldots\right)=\frac{1}{4}\left(\log_e n+\gamma+\log_e\frac{32}{\pi}\right)$$
$$-\left(\frac{3}{2}\beta T_3-\frac{3\,.\,5}{2\,.\,4}\beta^2T_5+\ldots\right). \quad . \quad (23)$$

when the value of c_n in (13) is introduced. This gives to $a-1$ the form stated above.

A convenient way of dealing with (C) is to take it in conjunction with (A), viz. add (C) to the result of dividing (A) by $2a$; which has the effect of giving to $(1+a^2+b^2-2a\cos\theta_r)^{3/2}$ a numerator $a+a^{-1}-2\cos\theta_r$, which to a

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close approximation is $2(1-\cos\theta_r)$. Thus in lieu of (C) we have

$$m_1\omega^2 a/\epsilon^2+\frac{c_n}{4a}+\frac{c_n}{2a^2}=-\sum_{s=1}^{s=n-1}\frac{a(1-\cos\theta_s)}{(2a^2+4b^2-2a^2\cos\theta_s)^{3/2}}$$
$$+\sum_{r=0}^{r=n-1}\frac{2(1-\cos\theta_r)}{(1+a^2+b^2-2a\cos\theta_r)^{3/2}}.$$

The results of previous summations now give when $a=1$ a value

$$m_1\omega^2/\epsilon^2=c_{2n}-\frac{9}{4}c_n+\frac{n}{2\pi}\left(\frac{3}{2}\beta S_3-\frac{3\,.\,5}{2\,.\,4}\beta^2 S_5+\ldots\right)$$
$$-\frac{2n}{\pi}\left(\frac{3}{2}\beta T_3-\frac{3\,.\,5}{2\,.\,4}\beta^2 T_5+\ldots\right)$$
$$=\frac{n}{4\pi}\left[\log_e(128\pi)-\gamma-\log_e n+2(\tfrac{3}{2}\beta S_3-\&c.)\right.$$
$$\left.-8(\tfrac{3}{2}\beta T_3-\&c.)\right]. \quad (24)$$

Thus it appears that when the numerical value of β is found, we have a given by (23), b by the definition of β as $b^2n^2/a\pi^2$, and ω by (24).

The solution of (22) proves to be less difficult than it appears. The numerical series denoted by S and T have values greater than 1 by amounts which converge rapidly as the suffix is increased, viz. with $S_3=1+S_3'$, ...

$$\left.\begin{array}{l} S_3'=\cdot 20206,\ S_5'=\cdot 03693,\ S_7'=\cdot 00835,\ S_9'=\cdot 00201, \\ \qquad\qquad\qquad\qquad\qquad\qquad S_{11}'=\cdot 00049,\ \ldots\ldots \\ T_3'=\cdot 05180,\ T_5'=\cdot 00452,\ T_7'=\cdot 00047,\ T_9'=\cdot 00005,\ \ldots \end{array}\right\} \quad (25)$$

With $\beta<1$,

$$S_3-\tfrac{3}{2}\beta S_5+\ldots=\frac{1}{(1+\beta)^{3/2}}+S_3'-\tfrac{3}{2}\beta S_5'+\frac{3\,.\,5}{2\,.\,4}\beta^2 S_7'+\ldots,$$

and so (22) stands

$$\frac{6}{(1+\beta)^{3/2}}+8(T_3'-\tfrac{3}{2}\beta T_5'+\ldots)=\frac{1}{\beta^{3/2}}+2(S_3'-\tfrac{3}{2}\beta S_5'+\ldots). \quad (26)$$

If the residual series are neglected, $6^{2/3}\times\beta=1+\beta$ or $2\cdot 302\beta=1$ or $\beta=\cdot 4344$. The difference of the residues proves small, and a corrected value is $\beta=\cdot 4308$. With

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this, and again making use of $S_3 = 1 + S_3'$, we obtain

$$\left.\begin{aligned} S_3 - \frac{3}{2}\beta S_5 + \ldots &= \cdot 7651, & T_3 - \frac{3}{2}\beta T_5 + \ldots &= \cdot 6333, \\ \frac{3}{2}\beta S_3 - \frac{3\,.\,5}{2\,.\,4}\beta^2 S_5 + \ldots &= \cdot 5337, & \frac{3}{2}\beta T_3 - \frac{3\,.\,5}{2\,.\,4}\beta T_5 + \ldots &= \cdot 4477. \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (28)$$

With these values, (23) becomes

$$\frac{2n^2(a-1)}{\pi^2} \times \cdot 6333 = \tfrac{1}{4}\log_e n + \cdot 2768,$$

or

$$n^2(a-1) = 1\cdot 948 \log_e n + 2\cdot 157, \quad . \quad (28)$$

and (24) is

$$m_1\omega^2/\epsilon^2 = \frac{n}{4\pi}(2\cdot 9053 - \log_e n) = \mathrm{N} \text{ say.} \quad . \quad . \quad (29)$$

§ 12. The equations (23) and (24) may be corroborated by use of the equation $2K + P = 0$, connecting kinetic and potential energies. The attraction section of P which contributes the positive element to 2K, that is to $2nm_1\omega^2a^2$, has a term ϵ^2 multiplied by

$$2n \sum_{r=0}^{r=n-1} (1 + a^2 + b^2 - 2a\cos\theta_r)^{-\frac{1}{2}}, \text{ or } 2n\,\Sigma\,(4a\sin^2\theta_r/2 + b^2)^{-\frac{1}{2}},$$

or

$$\sum_{r=0}^{r=n-1} n\left[\operatorname{cosec}\theta_r/2 - \frac{1}{2}\left(\frac{b}{2}\right)^2 \operatorname{cosec}^3\theta_r/2 + \ldots\right],$$

which is

$$n\left[2(c_{2n} - c_n) - \frac{4n}{\pi}\left(\frac{\beta}{2}T_3 - \frac{1\,.\,3}{2\,.\,4}\beta^2 T_5 + \ldots\right)\right] . \quad . \quad (30\,a)$$

With the opposite sign is a repulsive term,

$$-n \sum_{s=1}^{s=n-1} (2a^2 + 4b^2 - 2a_1^2\cos\theta_s)^{-\frac{1}{2}},$$

or

$$-nc_n + \frac{n^2}{\pi}\left[\frac{1}{2}\beta S_3 - \frac{1\,.\,3}{2\,.\,4}\beta^2 S_5 + \ldots\right]; \quad . \quad . \quad (30\,b)$$

with which is associated

$$-n/2b \quad \text{or} \quad -n^2/2\pi\beta^{\frac{1}{2}}. \quad . \quad . \quad . \quad . \quad (30\,c)$$

For the repulsive potentials of elements in the same circle there is division by 2 as well as multiplication by n, with a result

$$-\frac{nc_n}{2}\left(1 + \frac{2}{a}\right). \quad . \quad . \quad . \quad . \quad . \quad (30\,d)$$

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Thus finally for $a=1$, we get

$$m_1\omega^2 = c_{2n} - \tfrac{9}{4}c_n - \frac{n}{4\pi\sqrt{\beta}} + \frac{n}{2\pi}\left(\frac{1}{2}\beta S_3 - \frac{1.3}{2.4}\beta^2 S_5 + \ldots\right)$$
$$-\frac{2n}{\pi}\left(\frac{1}{2}\beta T_3 - \frac{1.3}{2.4}\beta^2 T_5 + \ldots\right). \quad (31)$$

If we subtract this from (24) we find a difference

$$\frac{n}{4\pi\sqrt{\beta}} + \frac{n\beta}{2\pi}(S_3 - \tfrac{3}{2}\beta S_5 + \ldots) - \frac{2n\beta}{\pi}(T_3 - \tfrac{3}{2}\beta T_5 + \ldots),$$

the vanishing of which constitutes the equation (22).

§ 13. The distinctive feature of the results is the appearance of a negative coefficient for the term $\log_e n$ in (29), which gives a termination to the series and at the same time leads to certain maxima and minima. We find, in fact:

(*a*) ω^2 vanishes for $\log_e n = 2{\cdot}9053$, that is for $n = 18{\cdot}3$.

(*b*) $\frac{dN}{dn} = 0$ for $\log_e n = 1{\cdot}9053$ or $n = 6{\cdot}72$, giving a maximum for N and, when the quantum condition is applied, a minimum for r_1.

(*c*) $\frac{d}{dn}(nN^2) = 0$ for $\log_e n = 2{\cdot}2386$ or $n = 9{\cdot}31$, giving a maximum value of K.

(*d*) $\frac{d}{dn}(nN) = 0$ for $\log_e n = 2{\cdot}4053$ or $n = 11{\cdot}1$, giving a minimum for the distance between the planes, as we proceed to explain.

If the quantity β defined by $n^2b^2/a\pi^2$ is to be treated as a pure number, then when distances $(r_2\, r_1\, z)$ replace $(1, a, b)$ we must suppose that $\beta\pi^2 = n^2b^2/a$ is replaced by

$$\beta\pi^2 = n^2z^2/r_1r_2, \quad \text{or} \quad z^2/r_1^2 = \beta\pi^2/an^2. \quad . \quad . \quad (32)$$

As $r_1^{-1} \propto N$, it is clear that $z^{-1} \propto nN$.

The magnitude of the shortest distance between elements is a matter of some importance in a nuclear system of this kind. Between positive elements that distance is $2z$, or when ratios only are concerned $2b$; and when n is great the distance between a positive and the nearest negative electron is approximately $\sqrt{b^2 + a^2\pi^2/n^2}$. Now

$$4b^2 : b^2 + a^2\pi^2/n^2 = 4\beta : \beta + a = 4\beta : \beta + 1$$
$$= 1{\cdot}7232 : 1{\cdot}4308 = 1{\cdot}204.$$

For higher values of n the distance between next adjacent

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positive and negative elements is about 9 per cent. less than $2z$ the distance between extreme planes. For helium we have $4b^2 : 1+a^2+b^2=1{\cdot}124$, and the shortest distance is about 6 per cent. less than the distance between extreme planes. As this is a small variation, a value of $2z$ may be taken as giving a sufficient clue to the magnitude of the shortest distance between elements.

§ 14. The difficulty in constructing a table of values, say for the primary series, lies in the fact that an asymptotic formula cannot be expected to give good values for small numbers, and the independent numerical solutions extend only to $n=4$.

On comparing the values of a and b (the latter through the β connexion) given by the asymptotic formulæ with the solution for $n=4$, the value of a is less than ·2 per cent. in excess, that of b less than ·5 per cent. in excess, of values obtained by solution. These are conspicuously favourable results, but the formula gives values 16 per cent. in defect for the value of ω^2, largely due to writing $a=1$ in the formulæ of approach to (29). The weakness occurs in a vital point, since the coefficient in the value of ω^2 determines the scale of dimensions when the quantum method is applied.

Attention will be given to a partial correction for values of n near the conclusion of the primary series, for which ω^2 is small, and so any terms neglected become of special importance. If in the terms containing c^n we do not write $a=1$, we shall obtain

$$m_1\omega^2a^3/\epsilon^2=c_{2n}\sqrt{a}-c_n(1+\tfrac{1}{2}\sqrt{a})^2+\text{series in }\beta:$$

it is proposed to examine the increment in the terms written. To the first order in $(a-1)$ they are:

$$c_{2n}-\tfrac{9}{4}c_n+\tfrac{1}{2}(c_{2n}-\tfrac{3}{2}c_n)(a-1)$$

or

$$c_{2n}-\tfrac{9}{4}c_n+\frac{n(a-1)}{4\pi}\left(\log\frac{32n}{\pi}+\gamma\right). \quad . \quad . \quad (33)$$

The first descending term in c_n is $\pi/72n$, which gives a correction $7\pi/144n$ to be applied to $c_{2n}-\frac{9}{4}c_n$. We also find for

$n=18$,	$a-1=$·024,	original N	·0213,	addition to N	·2056,	corrected N	·227	
„ 19,	„ ·022,	„	−·0593,	„	·1971,	„	·138	} ,
„ 20,	„ ·020,	„	−·1438,	„	·1914,	„	·0476	

. . . (34)

in which it has been presumed that series in β are less seriously affected.

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We can now give a short table of initial and final terms for the primary series.

n.	a.	N.	r_1.	$2z$.	κ.
2	1·888	·4560	6·338	8·972	2·195
3	1·468	·5424	5·328	5·914	4·669
4	1·301	·5752	5·024	4·524	7·001
.....	.....	.....	.....	.....	.....
18	1·024	·227	12·73	2·88	4·91
19	1·022	·138	20·94	4·44	1·91
20	1·020	·0476	60·7	12·40	·24

In this table

(1) a is the ratio of radii $r_1 : r_2$;

(2) the distances r_1 and $2z$ are the digits given with a factor 10^{-12};

(3) the kinetic energy $= m_1 V^2 \times 10^{-5} \times \kappa$, where κ is the number in the last column.

§ 15. It is proposed to state briefly the asymptotic position in reference to other series.

For (ii.) the right-hand member of (23) would contain an extra term $-\pi/2n$, and that of (22) an extra term $-\pi^2/n\sqrt{\beta}$, both of an order neglected in the work for (i.).

The alteration in ω^2 is on a higher scale, and is most readily found by the method of § 12.

The terms added to potential energy are $-2n\epsilon^2(a^2+b^2)^{-\frac{1}{2}} + n\epsilon^2$, and therefore the terms added to $m_1\omega^2 a^3/\epsilon^2$ or to $m_1\omega^2 r_1^3/\epsilon^2$, that is to N, have a value $a(a^2+b^2)^{-\frac{1}{2}} - a/2$, which approaches the limit 1/2 when n is increased.

In series (iii.) there is a new variable c, with an equation

$$\frac{n(c+b)}{(a^2+\overline{c+b}^2)^{3/2}} + \frac{n(c-b)}{(a^2+\overline{c-b}^2)^{3/2}} = \frac{nc}{(1+c^2)^{3/2}} + \frac{1}{4c^2}, \qquad (35)$$

required to secure the equilibrium of axial negative electrons. With b/c assumed to be negligible and $a=1$ this equation is reduced to $nc(1+c^2)^{-3/2} = 1/4c^2$, or approximately $c^3 = 1/4n$, a value which makes b/c of order $n^{-2/3}$.

Again, in (B) we have extra terms $(b-c)(a^2+\overline{b-c}^2)^{-3/2} + (b+c)(a^2+\overline{b+c}^2)^{-3/2}$, in which the main contributions of the c terms are cancelled and $2b$ is an approximate value, small in comparison with the term $1/4b^2$. The alterations to b and a, the latter judged as above for (ii.), are then small.

The potential energy has extra terms $-2n\epsilon^2/\sqrt{a^2+\overline{c-b}^2} - 2n\epsilon^2/\sqrt{a^2+\overline{c+b}^2} + 2n/\sqrt{1+c^2} + \epsilon^2/2c$, contributing to the

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value of $-2K$ or $-2nm_1\omega^2a^2$. Thus an approximate value of the terms added to N is $1/\sqrt{1+c^2}-1/4nc$, or $1-c^2/2-1/4nc$, or $1-3/8nc$, or $1-\frac{3}{8}\times\left(\frac{2}{n}\right)^{2/3}$.

Lastly, in series (iii.) as modified by a positive electron at the centre, the equation (35) is replaced by

$$\left.\begin{aligned}&\frac{1}{c^2}+\frac{n(c+b)}{(a^2+c+b^2)^{3/2}}+\frac{n(c-b)}{(a^2+c-b^2)^{3/2}}=\frac{1}{4c^2}+\frac{nc}{(1+c^2)^{3/2}},\\ &\text{or when } b/c \text{ is negligible,}\\ &\qquad\frac{3}{4nc^3}+\frac{2}{(a^2+c^2)^{3/2}}=\frac{1}{(1+c^2)^{3/2}}.\end{aligned}\right\}\quad(36)$$

This equation requires

$$(a^2+c^2)^{3/2}>2(1+c^2)^{3/2}\quad\text{or}\quad a^2-\sqrt[3]{4}>c^2(\sqrt[3]{4}-1),$$

that is $a^3>2$.

In the primary series, as n is increased a approaches 1 as limit; I have no doubt this is valid with any finite modification such as we are considering, and draw the conclusion that the series is of limited extent. In the primary series the value of a is already below the limit $a^3=2$ when $n=5$, but in this modification the position is more favourable, as giving $a=1{\cdot}803$ for $n=3$ while $a=1{\cdot}468$ in (i.).

The series is then probably confined to the cases $n=3$ to $n=5$, and its three examples have $p=7$, $q=2$; $p=9$, $q=3$; $p=11$, $q=4$.

§ 16. The three series cover only a moderate section of the whole range of atomic numbers.

The limitation in (i.) and the extensions provided in (ii.) and (iii.) point to the need of a stronger attracting force on the positive elements; or we may say that the demand is for a higher ratio of negative elements to positive than 1 : 2. We have reached the limit of negatives which can be added in special positions, and if the problem can be dealt with by addition to the main structure that addition must contain positive as well as negative elements. It is proposed to consider such an addition in the form of the double ring which was the subject of my earlier work, and to suppose it placed in the central plane inside the main structure. The proposal will be examined under two aspects—adaptation to given atomic weight and number, and capacity to provide attraction on the positive rings of the triplane.

If m is the number of positive or negative elements in the double ring, then $p=2n+m$ and in series (i.), (ii.), (iii.)

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n has the respective values q, $q+1$, $q+2$. As example *, take the case of Ag where $q=47$, and Aston gives 107, 109 as ascertained values of p. The arrangement for $p=107$ shows $m=9$, $n=49$ in (iii.), $m=11$, $n=48$ in (ii.), $m=13$, $n=47$ in (i.). An increase of m by 2 is needed to pass to the case $p=109$. If a minimum value of m is taken, series (iii.) appears in both cases; and then isotopes have the same n, but are distinguished by the use of different values of m.

In the matter of providing attraction for the positive elements of the triplane, (iii.) should be more efficient than (ii.), and (ii.) than (i.), since a position of negative electrons on the axis or at the centre assists in giving an external position to the negative ring in the double ring (*v. infra*). Thus, for large values of n at any rate, (iii.) only is likely to appear and one combination corresponds to one isotope.

The central double ring may be expected to make its appearance on the completion of the original series, beginning with $m=2$ and gradually requiring higher values of m. The case $m=1$ I refer to the heading (a) of § 5, which is or may be operative from $n=3$ forwards within the range of the original series.

§ 17. We consider now in general terms the mutual action of the double ring and the triplane.

The double ring alone (*i. e.* under no external force) is a plane structure with positives in the outer circle, with radii tending to equality as m is increased, and with a value of $m_1\omega^2a^3/\epsilon^2$ approaching a limit $m\times\cdot441$ or $2m\pi^{-1}\log_e 2$.

For a combination of the two types occurring first as n approaches a value 30, the action of the triplane on interior electrons does not differ much from that of a single ring of n positive electrons in the central plane. It tends to draw the negative electrons of the double ring away from the centre and to push the positive towards the centre, an action which is aided in (ii.) and (iii.) by a central or two axial negatives. When the action is sufficient to place the circle of negative electrons in the external position, the double ring exercises an attraction on the positive elements of the triplane, depending specially on m and on the difference of radii which the external force (of the triplane) is capable of securing.

The demand for attraction on the positive elements of the

* The only values to which I have access are those in 'Nature,' Sept. 22nd, 1923.

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triplane naturally increases as the number n increases. But whereas for small values of m a change in the ratio of radii is easy to bring about, it becomes increasingly difficult when m is greater and the relative closeness of elements gives to near neighbours a controlling influence on the ratio. Thus we should expect to find, as n is increased, a demand for a more than proportionate increase in m. We do, in fact, find that in the range $q=31$ to $q=47$, if a like choice of arrangements (in respect to series used) is made, m increases by 6 while n increases by 16; whereas later the increments become more equal, and finally that of m exceeds that of n or q.

Again, the action of the double ring on the two positive rings of the triplane tends to make the latter approach, and so to diminish the number β. This has the effect of increasing the number 2·905 in N, *cf.* (24) and (29), which was obtained by subtracting terms in the β section from $5{\cdot}42-\log_e n$. The amount subtracted would be diminished, and thus further aid given towards increasing the value of N.

These arguments are qualitative, and point to the action being in the sense requisite to make the scheme of completion feasible. Whether its intensity is adequate, only calculation can show: possibly the nature of the co-ordination of the two sections would be revealed in the course of adjustment of numerical values.

As with the primary series and its two extensions, so with this new addition it would appear probable that a terminus will be reached beyond which no construction of the type is valid.

§ 18. The existence of the atom in the shape of nucleus and satellites indicates a greater difficulty in incorporating negative electrons in the structure of the nucleus than in attaching them at relatively great distances; so that the former process is carried only so far as may be needed to overcome the mutual repulsion of positive elements. This feature is, I think, to be connected with the very different mean velocities of positive and negative electrons in a space where both are sparsely distributed. The accumulation of a positive residue in the nucleus tends to counteract this influence by providing an attraction for negative as against repulsion for positive electrons outside.

If we suppose that in such a space pairs are formed in a number of cases, then positive and negative free electrons are in the same position as regards attraction to a pair,

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supposing them to pass near to one or other member of the pair. But in the case of the positive electron the average relative velocity is on a smaller scale than for the negative, and there is a longer period of contiguity in which the attraction is effective. The combination of two positives at the end of a diameter with a negative at the centre is therefore more probable than the contrary arrangement, and special prominence attaches to the triplet * (2+, 1−).

But further steps are more conjectural. The readier attachment of members having moderate or small relative velocity would, if pairs were fairly numerous, suggest the formation of a linear series of pairs (or linear series of alternate + and −), where a considerable approach to equilibrium of forces would be attainable except at the terminals, which might be supposed to swing round so as to form a closed circuit. In like manner from a formation resembling the lattice model of two positives to one negative, the same failure in adjustment near the terminals might lead to the closure of the circuit giving the triplane model. The process of completion would be aided by the near presence of a double ring.

In one of these processes of aggregation a pair is the basic element; in the other, a triplet. The former yields a neutral structure which appears to have no permanent independent existence, unless we suppose it to have escaped detection. What advantage has the one type, or what special disability the other, to account for a difference in probability of existence? The slower velocity of translation in the heavier triplet forms gives greater opportunity for the formation of triplet configurations. The disability may be connected with a tendency of the double ring to attract slowly moving positive electrons within its inner (negative) ring. A formation with a negative ring between two positives *in a plane* is certainly less stable than the structure which has both positive rings in the outer position (as in the triplane), for in the latter less kinetic energy is needed to correspond to a given angular momentum. In virtue of this tendency the double ring may function as a stepping stone to the triplane model.

The disparity in mass between positive and negative

* The other form of triplet, with two positives at the base of an isosceles triangle and a negative at the vertex, may arise from two pairs by supposing a quicker response to repulsion on the part of the negatives, whereby one negative is left to prevent the separation of positives.

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electrons makes the latter take the inner place (where the field of force is small), either in the double ring or in the triplane, where nearly equal accelerations are attributed to the two. Kinetic theory connects disparity in velocity of translation with that in mass, and an imperfect attempt to trace this influence has been made in this paragraph. There may be a measure of crudity in thinking of a process of aggregation in this way, but it seems easier to conceive than an addition to a circuit already closed.

XLVIII. *The Partial Tones of the Struck String.*—Part I. *Experimental Investigation of the Fundamental.* By

Wm. H. George, *M.Sc., University College, Nottingham* *.

[Plates XIII.–XVI.]

Summary.

By harmonic analysis of photographically obtained vibration-curves of the struck string it is found that: (i.) the amplitude of the fundamental is greatest when the string is struck near one of the bridges; (ii.) the position of this maximum point is nearer the bridge the greater the relative mass of the hammer; (iii.) there are other maxima and minima, which become fewer and less pronounced as the relative mass of the hammer is reduced until for the mass-ratio $m/M = 1/2{\cdot}53$, there is only one minimum and two maxima for the whole length of the string; (iv.) the maxima are greater and the minima are less the nearer they are to a bridge.

It is well known that in a pianoforte the strings are struck near one of the bridges, but the reason for this is not established. The position of the impact has a strong influence on the duration of the impact and upon the pressure law of the impact, and it therefore plays an important part in determining the intensities of the partials in the resulting free vibrations of the string.

In the earliest treatment of the struck string, Helmholtz ('Sensations of Tone,' p. 79 and Appendix v.) was able, by the aid of various assumptions, to determine the amplitudes of the partial tones. Numerical values for five different cases are given, but there is no account of quantitative experimental work undertaken to compare theoretical and experimental values. Helmholtz found, theoretically, that if a string be struck at $1/n$ of its length from one of the bridges then the nth partial would be absent from the resulting free vibrations. He therefore concluded that an

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essential advantage in striking the pianoforte string at 1/7 to 1/9 was that the inharmonic 7th and 9th partials disappear, or at least become very weak.

As early as 1884, A. J. Hipkins (Proc. Roy. Soc. vol. xxxvii. p. 363), and, again, later (*ibid.* vol. xxxviii. p. 83), showed that if a string is struck at 1/8 the eighth partial is not absent. At this time, however, photographic methods of recording the vibrations of any point of the string were not available, and the human ear, often aided by resonators, was largely relied upon to judge the relative intensity of any partial.

The earliest quantitative experimental work was done by Kaufmann (*Wied. Ann.* 1895, vol. liv. pp. 675–712), whose very important paper deals chiefly with the pressure-time law of the impact. He also gives a graphical method for finding the vibration-curve of any point of the string for cases where the pressure law of the impact is known. The graphical method is used because the well-known analytical method would lead to very complicated equations. Included in the experimental work is a set of twenty-six vibration-curves, half of which record the motion of the mid-point of the string, and the other half record the motion of a point of the string distant one-third of its length from the bridge. The string was struck at each of thirteen equidistant points along its length. As a result of these and other experiments, Kaufmann concluded that when the string was struck at about 1/7 to 1/9 of its length the tone was strongest and fullest.

Theoretical work, similar to that of Helmholtz, was later carried out by Delemer (Sci. Abs. A, vol. ix. p. 623, 1906) and by Lamb ('Dynamical Theory of Sound,' p. 74, 1910), who each used different expressions for the pressure-law of the impact. Here, again, no experimental results were given.

In the present work an attempt has been made to systematically investigate the influence of the striking place upon the amplitudes of the partials. As will be seen from the curves, it was also found necessary to study the influence of the relative mass of the hammer. The photographic curves have so far been analysed for the *fundamental* tone only. Whilst the work was in progress a paper by S. K. Datta, on the Das Theory of the Struck String (Proc. Ind. Ass. vol. viii. part ii. 1923) was published. This deals with the mass ratio of hammer and string $m/M = 1{\cdot}687$, and values of the amplitudes of the partials are given for the striking place at 1/9 and 1/10. Also the change in the amplitude

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of the fundamental as the position of the impact moves from a bridge along the string up to 1/4 of the length. The experimental method used consisted in measuring with a microscope the amplitude after the string had been struck at the particular place, and then damped at a suitable node for the desired partial. Account has to be taken of the fact that the damping eliminates only those partials which have not a node at the damped point, so that each microscope-reading represents a sum of a number of partials given by A_n, A_{3n}, A_{5n} . . ., etc.

Experimental Method.

In addition to the factors to be studied in the present work, it is clear that the absolute magnitude of the partials will depend upon

(i.) the tension of the string,
(ii.) the length (l) of the string,
(iii.) the velocity (v_0) with which the hammer strikes the string,
(iv.) the optical magnification,
(v.) the time which elapses between the impact and observation of the vibration.

This latter factor must be taken into account since in all practical cases damping is present to an unknown extent. The different partials may die away at different rates, so that it is not necessarily sufficiently accurate to take each record or observation at the same time after the impact.

The photographic records of vibrations reproduced in Plates XIII.–XVI. are all displacement-time curves obtained by shooting the plate upon which the shadow of one point of the string is optically projected.

The apparatus used has already been described in a previous paper (Phil. Mag., July 1924), and, since it includes a timing device, it was possible to obtain in each case a record of the *initial* free vibrations of the mid-point of the string. Some of the curves reproduced on a reduced scale in Plates XIII.–XVI. show even the initial motions, whilst the hammer is still in contact with the string. Errors due to variations of the fifth factor mentioned above are therefore eliminated. By using for any given series of observations the same length of string tuned to the same pitch, the first two factors are kept constant. The third factor, the velocity (v_0), with which the hammer strikes the string, is kept constant by allowing the hammer

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to fall always from rest at the same initial inclination (β) with the vertical. From time to time throughout a series of observations, when the initial conditions are shown upon the photographic plate v_0 can be determined from the expression $v_0=(V \tan \alpha)/(\text{magnification})$, and the result compared with the theoretical value given by $v_0=\sqrt{2gr(1-\cos \beta)}$, where (V) is the velocity of the plate in the vibration camera, (α) is the inclination with the time axis of the initial motion of the observed point of the string, and (r) is the distance between string and axis of rotation of the pendulum. Reference will later be made to the fourth factor, the optical magnification.

The two factors studied throughout this work were the mass of the hammer (m) and the position of the impact (a). By the term "mass of hammer" is here meant the mass of a particle equimomental with the compound pendulum which formed the hammer, so far as rotation about the axis of the pendulum at a distance (r) from it was concerned. The quantity was calculated from the weights and measurements of the complete hammer. The position of the impact (a) was measured by first smoking the string and allowing the hammer to strike once only. The bright speck caused by the removal of the black deposit at the place of impact left a clearly defined mark, from which the distance of the bridge was measured. When the larger string was used (316 cm.) this precaution was not necessary in order to get (a) with sufficient accuracy.

Analysis of Curves.

By recording the vibrations of the mid-point of the string the even-numbered partials were already eliminated from the curves.

Mader Harmonic Analyser.—The results given in Tables I. and II. were obtained by means of the Mader Harmonic Analyser. Before this was possible, the curves had to be enlarged. Now the time axis, which determines the wave-length of the curve, depends upon the speed with which the plate is shot in the vibration camera, and is independent of the optical magnification. On the other hand, the amplitudes of the partials depend on the optical magnification, but are independent of the speed of the plate in the camera. It is clear, then, that all the curves must be magnified by the same amount, and not so as to have the same fundamental wave-length. The Mader Harmonic Analyser was specially convenient for this work, since its readings are

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independent of the wave-length of the fundamental provided the curve is properly fixed relative to the instrument and the tracer correctly set upon the tracing-arm before tracing each curve. Each of the original curves reproduced in Plate I. was projected on to a screen and traced by hand, the final wave-length of the fundamental being about 32 cm. in each case. The curves reproduced in Plate XIV. were similarly treated, but, since the pitch of the string was higher, the final wave-length in the curves used on the analyser was about 14 cm. The readings of the sine (S_1) and cosine (C_1) components of the fundamental given in Tables I. and II. are each the mean of three readings, the

TABLE I.—Amplitude of Fundamental (A_1).

Wedge-shaped Metal Hammer $m/M=1$; Length of String (l) = 316 cm.

Number of Fig. (Pl. XIII.).	a in cms. = Point Struck.	S_1 = Mean Sine Component.	C_1 = Mean Cosine Component.	$A_1 = \sqrt{S_1^2+C_1^2}$.
1	11·0	+2·065	+1·005	2·297
2	14·37	+2·89	+0·635	2·959
3	16·1	+3·16	+0·505	3·[illegible]00
4	20·3	+3·792	+0·07	3·793
5	28·3	−4·685	+0·41	4·703
6	34·4	−4·793	+0·05	4·793
7	41·6	−5·235	−0·078	5·236
8	48·2	+5·33	+0·435	5·348
9	53·6	+4·97	+0·093	4·972
10	62·4	+4·093	+0·02	4·090
11	69·7	−2·91	+0·135	2·913
12	75·5	+2·395	+0·246	2·407
13	81·75	−1·935	−0·61	2·029
14	86·75	−1·413	−0·08	1·415
15	92·0	−1·01	+0·10	1·015
16	97·0	+1·066	−0·10	1·071
17	100·0	+1·17	+0·03	1·171
18	105·3	−1·79	−0·12	1·794
19	110·3	+2·445	+0·20	2·453
20	116·1	+2·52	−0·57	2·584
21	120·2	−2·42	+0·82	2·555
22	128·2	−2·73	+0·21	2·738
23	144·3	+2·613	−0·10	2·615
24	139·55	+3·02	−0·07	3·021
25	134·8	−2·865	+0·09	2·866

last column showing the amplitude (A_1) of the fundamental obtained by taking the square root of the sum of the squares of the sine and cosine components. The readings are in centimetres.

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TABLE II.—Amplitude of Fundamental (A_1).

Wedge-shaped Metal Hammer $m/M = 9{\cdot}625$; Length of String (l) = 100 cm.

Number of Fig. (Pl. XIV.).	a in cms. = Point Struck.	S_1 = Mean Sine Component.	C_1 = Mean Cosine Component.	$A_1 = \sqrt{S_1^2 + C_1^2}$.
1	1·43	−2·52	−0·34	2·54
2	3·52	−4·475	−0·035	4·475
3	5·58	−3·47	−0·13	3·47
4	6·37	+2·61	−0·01	2·61
5	7·27	−1·595	+0·02	1·59
6	8·20	−0·56	−0·125	0·57
10	10·6	+1·91	−0·07	1·91
11	11·7	−2·725	−0·16	2·73
12	14·0	−3·99	−0·15	3·99
13	15·18	−3·87	−0·15	3·87
14	16·3	−3·23	−0·08	3·23
15	17·75	−2·345	−0·26	2·36
16	19·94	−1·16	−0·05	1·16
17	22·6	−1·10	−0·805	1·36
18	25·05	−2·405	−0·005	2·405
19	27·8	−3·59	−0·40	3·61
20	30·6	−2·47	−0·19	2·48
21	33·58	−2·115	−0·09	2·12
22	36·9	−1·945	−0·03	1·95
23	41·9	−2·635	−0·265	2·65
24	50·0	+3·395	−0·65	3·45

Graphical Method.—The curves of Plates XV. and XVI. had previously been analysed by a graphical method, which consisted in removing the partials one at a time until the resulting curve looked like a pure sine curve. The amplitude of this remaining curve then gave the amplitude of the fundamental. To remove any given partial, a tracing of the vibration-curve was moved along the axis of the original curve a distance of *half* the wave-length of the partial which it is desired to remove. The ordinates were then added algebraically at a sufficient number of points, and the new curve drawn through these points represented the original curve with one partial removed.

RESULTS.

The results of four sets of analyses are best seen in detail in figs. 1–4, in which the amplitudes of the fundamental are plotted against the distance (a) of the striking place from the nearer bridge. For the heaviest hammer (see fig. 2)

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Fig. 1.

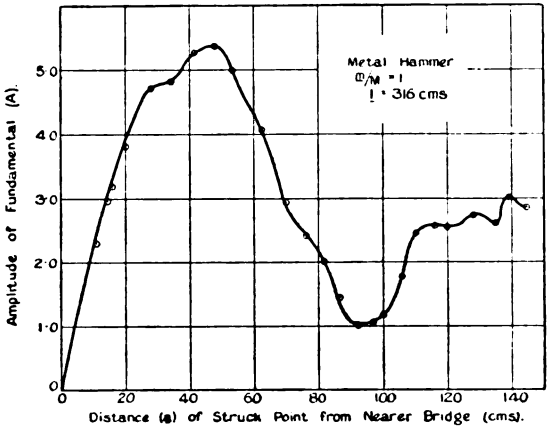

Fig. 2.

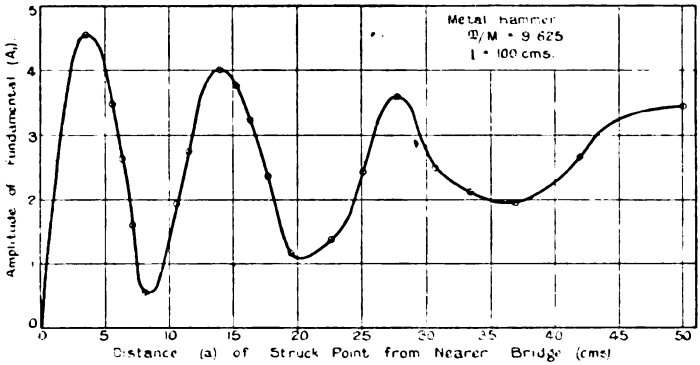

Fig. 3.

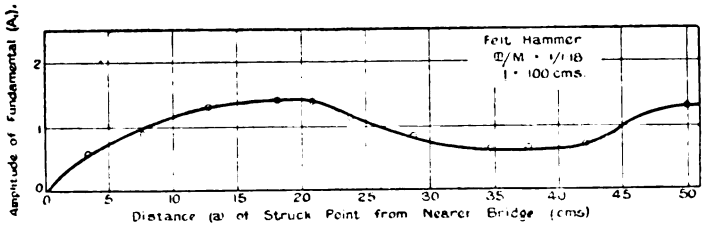

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Fig. 4.

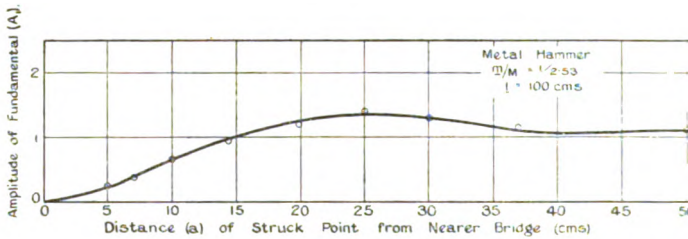
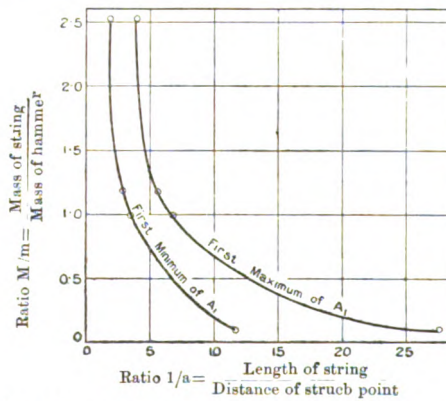


Fig. 5.

Influence of M/m upon positions of Struck Point for the first maximum and the first minimum values of the amplitude (A_1) of the fundamental.



there are for the whole string seven places at which the amplitude rises to well-marked maxima and six corresponding minima, whilst for the lightest hammer (see fig. 4) there are only two maxima and one minimum. The results may be summarized thus :—

(i.) The amplitude of the fundamental is greatest when the string is struck near one of the bridges.

(ii.) The position of this maximum point is nearer the bridge the greater the relative mass of the hammer (fig. 5).

(iii.) There are other maxima and minima points which become fewer and less pronounced as the relative mass of the hammer is reduced, until for the mass-ratio (m/M = 1/2·53) there is only one minimum and two maxima for the whole length of the string.

(iv.) The maxima are greater and the minima are less the nearer they are to a bridge.

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Attention is drawn to the figs. 7, 8, and 9 of Plate XIV., which show that the fundamental is hardly excited at all in these particular cases, and a change of 0·12 cm. in the position of the impact is sufficient to make an appreciable difference in the amplitude of the vibration (figs. 7 and 8). All the figures on this Plate, except figs. 4, 5, and 15, show the initial motions of the observed point. As the position of the impact gets nearer the observed point, the successive reflexions at the hammer during the impact can be seen. It is hoped that by the oscillograph method (see Roy. Soc. Proc. A, vol. cviii. pp. 284–295 (1925)) and the use of a carbon contact it will be possible to detect all the corresponding pressure-changes at the hammer under conditions like these.

In Part II. of this paper it is hoped to give the theoretical amplitudes of the partials derived by the well-known method (Rayleigh, 'Sound,' vol. i. § 130) and to compare these results with the experimental ones here given, the harmonic analysis of the curves being completed for the other partials.

University College,
Nottingham,
April 1925.

XLIX. *Notices respecting New Books.*

The Theory of Relativity. By L. Silberstein, Ph.D. Second Edition, enlarged. [Pp. x + 563 with 24 figures.] (London: Macmillan & Co., 1924. Price 25*s.* net.)

THE first edition of this work, published in 1914 and dealing with the restricted theory of relativity, is well known. This is reprinted with very few changes as Chapters I. to X. of the present book. In spite of the development of the tensor calculus, which forms a weapon of very great power for attacking the problems of generalized relativity, the author has adhered to the ordinary vector analysis and quaternions in dealing with the restricted theory. There is much to be said for this course; the older methods are amply sufficient for their purpose, and their physical interpretation is more easily comprehended by the beginner. Of the new matter in this edition, Chapters XI. to XIV. deal with the generalized theory and the crucial phenomena; Chapter XV. deals with the attempts of Weyl and others to bring electromagnetic phenomena into the generalized relativity scheme;

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and Chapter XVI. is devoted to cosmological speculations. A series of miscellaneous notes are added at the end, explanatory of, or supplementary to, various matters discussed in these chapters.

The treatment is admirably clear throughout. The author has been at considerable pains to distinguish between the metrical and non-metrical properties of tensors, and to make clear the physical meaning of the analysis and the results. Students of very modest mathematical attainments will therefore be able to read the volume with profit. The author avoids the paradoxical methods of presentation which have marred some treatments of the theory and which have increased the difficulties of the student. The treatment of the subject is in many respects novel, and it is evident that great care has been taken to minimize the difficulties—conceptual and analytical—of the theory.

The last chapter is the one in which there is the greatest divergence from other treatises on the theory. A detailed study is given of both Einstein's and de Sitter's cosmologies. The author explains clearly why, in his opinion, Einstein's cosmology is untenable. The generalized Doppler effect, due both to distance and to line-of sight motion, is explained in detail, and the radial velocities of special nebulæ are used to derive an estimate of the curvature radius of de Sitter's space-time. This portion of the subject is still very speculative, but the author's discussion appears to give substantial support to de Sitter's cosmology. We are grateful to the author for this detailed account of a part of the theory which has been much neglected.

Full references to original papers are given throughout.

In conclusion, we may say that we do not know a better or more complete exposition of the theory of relativity than that under review.

Introduction to Theoretical Physics. Volume I. By ARTHUR HAAS, Ph.D., Professor of Physics in the University of Vienna. Translated by T. VERSCHOYLE, M.C., B.Sc., A.R.C.S. [Pp. xiv+331 with 58 figures.] (London: Constable & Co., 1924. Price 21*s.* net.)

THE days when the various branches of physics could be treated as isolated units are long past. Modern physics is, however, such a vast subject that a text-book of reasonable size can deal with only one branch or portion of one branch. There is, therefore, a real need for a book in which the various branches of the subject are developed in connexion with one another and with a consistent notation. Such a volume can necessarily not be exhaustive, but should deal with fundamental principles in a stimulating manner so that the student or worker in other branches of science will have a well-balanced view of the whole subject and of the relationship of its different parts. Christiansen's

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'Elements of Theoretical Physics' was a book of this nature, but was published 30 years ago and is now in many respects out of date. All students of science should, therefore, be very grateful to Professor Haas not merely for filling this gap in scientific literature, but for filling it in such an excellent manner. A judicious selection of material, combined with a mathematical treatment in which successive steps are carefully explained, render the volume one which can be read with profit by the student of every branch of science, even though his mathematical equipment is of the slenderest.

At present only Volume I. is available in the English translation. It is to be hoped that Volume II. will shortly be published. The first volume is divided into two parts dealing respectively with mechanics, including the general theory of vector fields, of vibrations and of potential, and the theory of the electromagnetic field and of light. We are glad to see vector notation and analysis used from the beginning; frequently the student makes his first acquaintance with the vector notation when he begins to study the electromagnetic theory, whereas many problems in mechanics such as the rotation of a rigid body about a fixed axis lend themselves admirably to vector methods. Professor Haas has the happy gift of being able to condense a large amount of material in concise yet readable form, and it is surprising what a wide field is covered in about 300 pages. A summary of the contents is given at the end which is valuable not only for reference purposes, but also to enable the student more easily to trace the connexion between different portions of the argument.

The volume is one which can be thoroughly recommended to and should be read by every serious student of science.

The Principle of Relativity. A Collection of Original Memoirs on the Special and General Theory of Relativity. By H. A. LORENTZ, A. EINSTEIN, H. MINKOWSKI, and H. WEYL. With Notes by A. SOMMERFELD. Translated by W. Perrett and G. B. Jeffery. (Methuen: London. 12*s.* 6*d.*)

IT is a great convenience to have between one pair of covers the important original papers contained in this volume. There is first, part of the classical paper by Lorentz on Michelson's Interference Experiment, written in 1895, followed by his paper on Electromagnetic Phenomena in a system moving with any velocity less than that of Light, which appeared in 1904. Then come Einstein's papers on the Electrodynamics of Moving Bodies, which originally appeared in the *Annalen der Physik* in 1905, and his short paper on the Dependence of the Inertia of a Body on its Energy Content, published in the same issue of that journal. Next comes the paper by Minkowski on Space and Time, which will be for ever a classic, which he gave as an address

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to a congress of physicists in Cologne in 1906. There is a valuable appendix to this paper in the form of notes by Sommerfeld. Weyl is represented in this volume by a reprint of his paper on Gravitation and Electricity, from the *Sitzungsberichte der Preussischen Akad. d. Wissenschaften*, 1918.

The other half of the volume is wholly a reprint of Einstein's later papers. There is the paper on the Influence of Gravitation on the Propagation of Light, from the *Annalen der Physik*, 1911. Next, the Foundation of the General Theory of Relativity, from the same journal in 1916. Next there is the paper on Hamilton's Principle and the General Theory of Relativity, from the *Sitzungsberichte der Preussischen Akad. d. Wissenschaften*, 1906. Finally there are the papers originally published in this same journal in 1917 and 1919 respectively on Cosmological Consideration on the General Theory of Relativity, and the paper entitled "Do Gravitational Fields play an Essential Part in the Structure of the Elementary Particles of Matter?"

It will be seen that the contents of this book make it of the very greatest value as a convenient reference book for the progress of the theory of relativity in the work of Einstein through its first two stages. The addition of the other very important papers further increases its value. The translators are to be congratulated very heartily on their achievement.

Einstein's Theory of Relativity. By MAX BORN. Translated by H. L. Brose, M.A. (Methuen: London. 12*s*.)

THIS book is a translation of the third edition of Born's book which appeared originally in German in 1900. The idea of the book, according to the author, was to give an exposition of the Theory of Relativity *ab initio*, which could be followed by those who have very little knowledge of mathematics or physics. Professor Born set out on this rather formidable task by discussing at some length, with the help of a number of experiments, the classical conceptions of velocity, acceleration, mass, force, and so on. The reader is then brought by easy stages all the way to the general Theory of Relativity. Professor Born has evidently expended a great deal of care on developing all the points in the easiest and simplest fashion for the audience which he has in view, and those students who have an ambition to understand the Theory of Relativity in spite of a meagre equipment in mathematics and physics would find it worth while to study this book. The translation appears to be very satisfactory.

Space and Time. By CARL BENEDICKS. With an Introduction by Sir OLIVER LODGE. (Methuen. 4*s*.)

THIS small thin volume is an essay embodying Professor Benedicks's views on the foundations of new theories. His

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purpose is not to understand them in themselves, but to discuss how far they are necessary or not from the standpoint of science in general. The essay is based on an address given to the Students' Club in Stockholm, and though quite slight, it is interesting and well worth reading.

The History of Mathematics in Europe. By J. W. N. SULLIVAN. (Pp. 109, with 17 illustrations.)
Electricity and the Structure of Matter. By L. SOUTHERNS, M.A., B.Sc. (Pp. 128, with 34 illustrations.)
("The World's Manuals": Oxford University Press, 1925. Price 2*s.* 6*d.* net each).

THESE two volumes are included in a new series, entitled 'The World's Manuals,' which are in course of publication by the Oxford University Press. The series is designed to provide the student who is undertaking a special study with the broad outlines and guiding principles of his subject, and also to be of interest to the great body of general readers who welcome accurate and concise accounts of subjects of general interest. The two volumes under review are included in the section "Science and the History of Science." The first of the two is one of the subseries, "Chapters in the History of Science," the general editor of which is Dr. Charles Singer. It traces in outline the development of mathematics from its beginnings in Europe up to the time of the rise of the conception of mathematical rigour. The contributions by the principal mathematicians of the period covered are carefully summarized. Specimens of actual solutions of several problems (in modern notation) and also of notation from early mathematicians are given. These enable the reader more clearly to realize to how great an extent successive advances were dependent upon the improvement of the notation in use and the better to understand the quality of their achievements. The second volume gives a brief outline of the history of the subject dealt with up to the time of the discovery of the electron, followed by an account of some of the older and also of the principal modern applications and developments of electricity, both theoretical and practical. These include radio-activity, the structure of the atom, electromagnetic waves, and the use of X-rays for the study of crystal structure.

Both volumes are written in a scholarly manner and form concise and accurate summaries of the subjects dealt with. They can be thoroughly recommended both to the scientific and also to the general reader.

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L. *Intelligence and Miscellaneous Articles.*

THE CONSTANT N OF AVOGADRO.

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

I HAVE just read in the April issue of the Phil. Mag. the letter of Mr. L. M. Alexander, Assistant Professor of Physics in Cincinnati, concerning my paper "A New Determination of the Constant N of Avogadro," which was published in the Philosophical Magazine, 1924, xlviii. p. 664, and I wish to thank him for the opportunity that he gives me of correcting myself.

Of course, his criticisms of the two estimates of the per cent. error involved in the calculations are obviously true. But I did not say in my paper that my value and that of Millikan agreed within the experimental error, although the difference of 1 per cent. is small. Thus, one should read 1 per cent. instead of 0·1 per cent., and $\pm 0{\cdot}009$ instead of $\pm 0{\cdot}08$.

As to the third objection, which is also very obvious, it was not even necessary to use so many formulas to reach the conclusion that, having started from a value of the area obtained from the knowledge of A, surface of adsorption, one was bound, after cancellation, to reach the conclusion that $A = A$, unless the arithmetic had been wrong. Unfortunately, this identity did not strike me before the paper was out, and I plead guilty to the oversight. I may add that I corrected these three errors in a subsequent paper on the same subject, which I sent to the 'Journal de Physique,' and which was received in Paris on the sixth of January, 1925, long before I read Professor Alexander's letter. This paper is now in the press, and would have been out before if it had not been delayed by a printers' strike.

However, I wish to emphasize the fact that none of these errors invalidated in any way the experimental work, or the conclusions drawn from it.

I take this opportunity to correct another slight mistake which Professor Alexander has overlooked. The real value of N obtained from my experiments should read

$$N = 6{\cdot}004$$

instead of 6·003.

With many thanks for your courtesy, I remain

Yours very truly,

LECOMTE DU NOÜY.

The Rockefeller Institute,
New York,
May 28, 1925.

(P. Lecomte du Noüy, Sc.D.)

[*The Editors do not hold themselves responsible for the views expressed by their correspondents.*]

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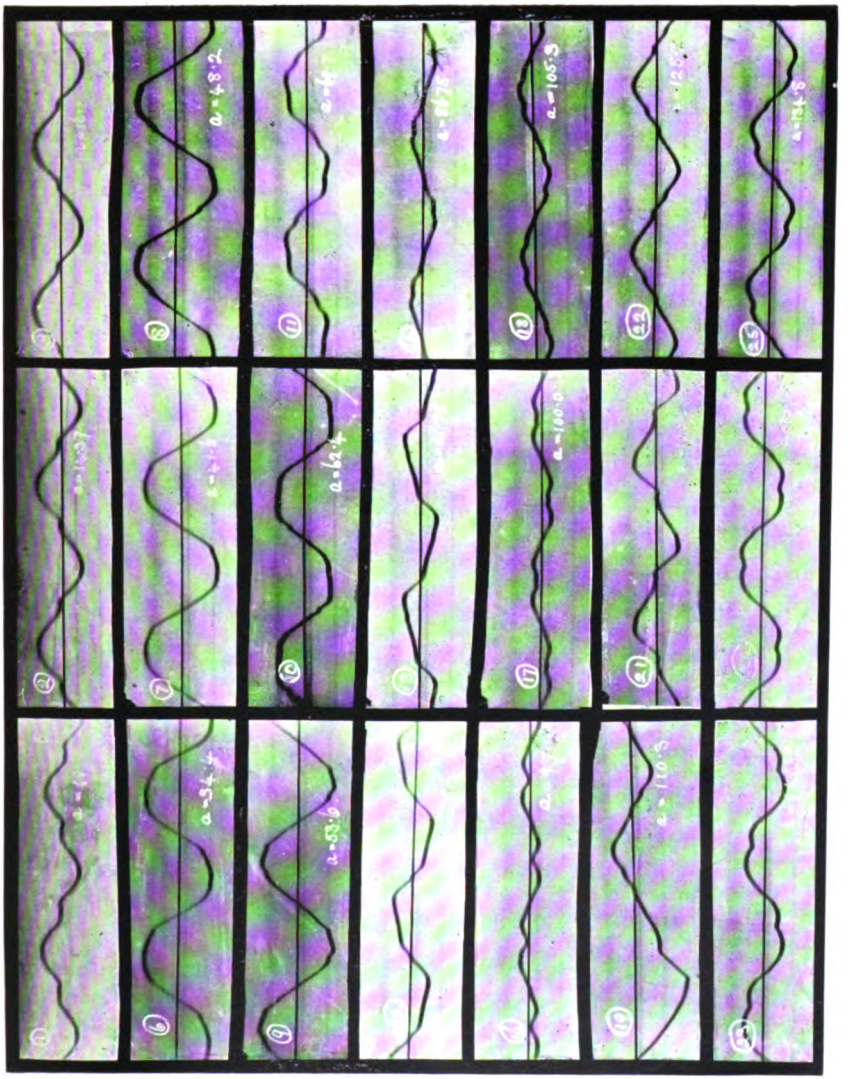

Vibration Curves of the Mid-Point of the String.

Metal Hammer $m/M=1$; $l=316$ cm.; a = Distance of Struck Point from Nearer Bridge; Linear Density (μ) of Wire = 0·093 gm. per cm.; Time Axis is Positive from left to right. Fig. 19 shows Initial Conditions.

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Vibration Curves of the Mid-Point of the String.

Metal Hammer $m/M = 9{\cdot}625$; $l = 100$ cm.; a = Distance of Struck Point from Nearer Bridge; Linear Density (μ) of Wire $= 0{\cdot}0174$ gm. per cm.; Time Axis is Positive from right to left. All figures except Nos. 4, 5, and 15 show Initial Conditions.

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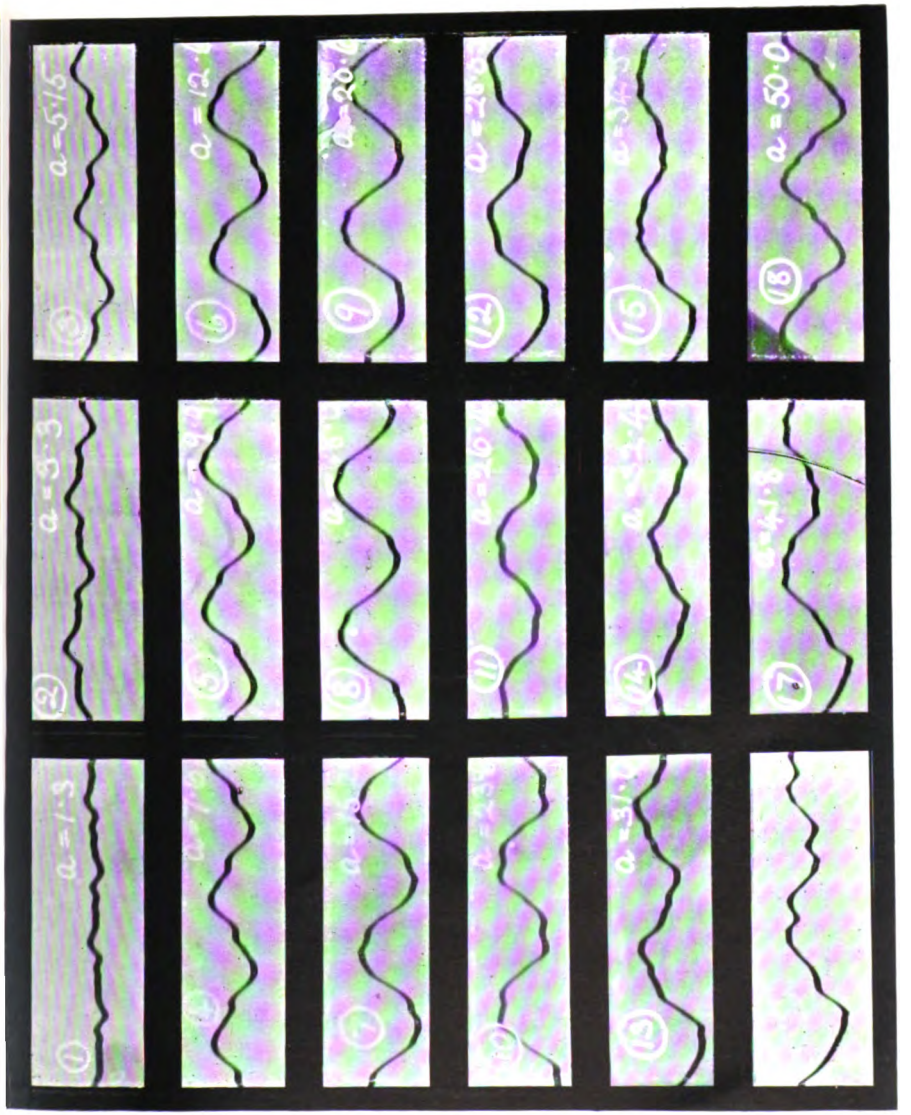

Vibration Curves of the Mid-Point of the String.

Felt Hammer $m/M = 1/1{\cdot}18$; $l = 100$ cm.; a = Distance of Struck Point from Nearer Bridge; Linear Density (μ) of Wire = 0·093 gm. per cm.; Time Axis is Positive from left to right. Initial Conditions can be seen in Figs. 5, 6, 8–13, 15–18.

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Vibration Curves of the Mid-Point of the String.

Metal Hammer $m/M = 1/2{\cdot}53$; $l = 100$ cm.; a = Distance of Sruck Point from Nearer Bridge ; Linear Density (μ) of Wire = 0·093 gm. per cm.; Time Axis is Positive from left to right. **Fig. 17** shows Initial Conditions.

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THE

LONDON, EDINBURGH, AND DUBLIN

PHILOSOPHICAL MAGAZINE

AND

JOURNAL OF SCIENCE.

[SIXTH SERIES.]

SEPTEMBER 1925.

LI. *On the Effect of Chemical Constitution on the X-Ray Spectrum of Sulphur.* By B. RAY, *D.Sc., Lecturer in Physics, Calcutta University* *.

[Plate XVII.]

§ 1. *Introduction and Experimental Results.*

As is well known, the phenomena of X-ray spectra are almost but not quite independent of the physical and chemical state of the element under investigation. This effect appears primarily in the wave-lengths of the absorption edges, and has been subject to a number of investigations in Professor Siegbahn's laboratory. As would be expected from theoretical considerations, the effect on the wave-lengths of the emission lines is much smaller. Still, a perceptible influence was detected in a recent investigation by the writer †, who, using the precision X-ray spectrograph of Siegbahn, was able to detect a small difference in the wave-lengths of $K\alpha_1$ and $K\alpha_2$ in a number of elements when investigated under different conditions. This difference was especially conspicuous in the distance between the two lines known as the relativity doublet, whereas the absolute shift of the lines was not determined with great accuracy. On account of the theoretical interest of the problem of the origin of this doublet, the writer has extended the investigation to the case of sulphur where, partly due to the

* Communicated by Prof. N. Bohr.

† Phil. Mag. Jan. 1925.

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variability of its chemical compounds and partly due to its small atomic number, large effects might be anticipated, and where the absolute as well as the relative shift could be determined more easily.

The apparatus used was a vacuum spectrograph with metal X-ray tube of Professor Siegbahn's construction. The high vacuum in the X-ray tube was separated from the low vacuum in the spectrograph by goldbeaters' skin. Since the sulphur rays are very easily absorbed in air, an auxiliary oil-pump was used to have the vacuum in the spectrograph as high as possible. The salt under investigation was pressed on the anti-cathode in the form of powder in the usual way. As is, however, well known, salts placed on the anti-cathode disappear rapidly and are apt to undergo chemical alterations, and a special type of anti-cathode was therefore used containing four faces, each of which was covered with salts at the beginning of the experiments, and one after the other could be exposed to the cathode rays by simply turning the anti-cathode from the outside in its vacuum-fitting. Another new addition to the spectrograph consisted in a metallic shutter placed just before the photographic plate but supported independently by the base of the spectrograph. This shutter, constructed by Mr. Olsen of this laboratory, allowed two exposures to be obtained on one and the same plate, one just above the other, without the risk of any shift in position of the plate. This was of special importance for the direct comparison of the spectra of the different sulphur compounds.

Calcite was used as a crystal, and in order to ensure sharp images the crystal was during the exposure slowly turned to and fro through an angle of about one degree.

In order to measure the wave-lengths of sulphur lines, the cobalt lines were taken as reference. In fact, the $K\alpha_1$ and $K\alpha_2$ lines of sulphur in the first order appear on the plate between the $K\alpha_1$ and $K\alpha_2$ lines of Co in the third order. The wave-lengths of the sulphur lines would therefore be obtained by interpolation from Siegbahn's precision measurements of the Co lines. As a check of this method, the said wave-lengths were also calculated by means of the distance from the photographic plate to the crystal, which for this purpose could be easily found with sufficient accuracy.

The results of the measurements are given in Table I. The accuracy in the measurements is generally of the order 0·06 X-unit. The second decimal has therefore been printed in small figures.

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TABLE I.—Wave-length in X-units.

Compound.	α_2.	α_1.
S	$5363{\cdot}8_5$	$5360{\cdot}9_1$
	$5363{\cdot}8_6$	$5360{\cdot}9_0$
	$5363{\cdot}8_7$	$5360{\cdot}9_0$
	$5363{\cdot}9_0$	$5360{\cdot}9_1$
	$5363{\cdot}9_1$	$5360{\cdot}9_1$
Mean ...	5363·90	5360·90
CaS	$5363{\cdot}9_0$	5360·90
FeS	$5363{\cdot}8_7$	,,
CuS	$5363{\cdot}9_0$	,,
SrS	$5363{\cdot}9_2$	,,
MoS	$5363{\cdot}8_6$	,,
Ag_2S	$5363{\cdot}9_1$	,,
SnS	$5363{\cdot}9_0$	,,
Sb_2S_3	$5363{\cdot}9_0$	,,
Sb_2S_5	$5363{\cdot}9_1$	,,
BaS	$5363{\cdot}8_7$	,,
PbS	$5363{\cdot}9_0$	,,
Mean ...	5363·90	
Na_2SO_4	5360·90	$5358{\cdot}5_1$
K_2SO_4	,,	$5358{\cdot}4_8$
$CaSO_4$	,,	$5358{\cdot}4_6$
$Fe_2(SO_4)_3$	,,	$5358{\cdot}5_3$
$CuSO_4$	,,	$5358{\cdot}4_6$
$SrSO_4$	,,	$5358{\cdot}5_0$
Ag_2SO_4	,,	$5358{\cdot}5_4$
$BaSO_4$	,,	$5358{\cdot}4_6$
$PbSO_4$	,,	$5358{\cdot}4_6$
	Mean ...	5358·50
Na_2SO_3	5360·90	$5358{\cdot}5_0$
$CaSO_3$	,,	$5358{\cdot}4_6$
$CuSO_3$	,,	$5358{\cdot}4_6$
Ag_2SO_3	,,	$5358{\cdot}4_8$
$CdSO_3$	,,	$5358{\cdot}4_8$
$BaSO_3$	,,	$5358{\cdot}5_0$
$PbSO_3$	,,	$5358{\cdot}5_3$
	Mean ...	5358·50

As will be seen, the values for the various types of compounds agree very closely with each other. As regards pure sulphur, no difference could be observed between rhombic and plastic sulphur. As seen from the table, also no difference could be ascertained between pure sulphur and sulphides of various metals. Similarly the values for the

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various sulphates and sulphites agree closely with each other. However, a very marked difference appeared between sulphur and sulphides on the one hand and sulphates and sulphites on the other. This difference consisted not only in a shift of the position of the doublet, but also in a change of its width. Thus, as a mean result of our measurements, we have found for sulphur or sulphides $\Delta\lambda = 3{\cdot}0$ X.U., and for sulphites or sulphates $\Delta\lambda = 2{\cdot}4$ X.U. The shift of the position of the whole doublet was so large that on the plates the $K\alpha_1$ line of sulphur coincided with considerable accuracy with the $K\alpha_2$ line of a sulphate. As a consequence of this, the plate will exhibit three lines instead of four when a mixture of sulphide and sulphate is present on the anti-cathode. Owing to the reduction of the salts under the bombardment of the cathode-rays, photographs of long exposures of sulphates or sulphites show besides two stronger lines also a third faint line at the position of $K\alpha_2$ for a sulphide. (See Pl. XVII. *a*, *b*, *c*, *d*.)

This observation raises the question as to the extent to which chemical changes on the anti-cathode may influence the results. Thus it might be imagined that the identity of the spectra obtained with sulphite or sulphate, or with sulphur or sulphide, is due to the one form being in a very short time converted into the other. However, no trace of additional faint lines could be observed, even if the material on the anti-cathode was frequently renewed.

Another interesting feature is exhibited by the lines $K\alpha_3$ and $K\alpha_4$. Their wave-lengths are always found to be the same whether they are excited in sulphur crystals or sulphides on the one hand or sulphites or sulphates on the other. The only difference lies in the fact that in the former case the lines are sharp, while in the latter case they are somewhat diffuse, the edge of the lines on the side of short wave-lengths being somewhat less sharp than the edge on the side of long wave-lengths. Although this want of sharpness is probably due to alterations in the chemical state, the experiments leave hardly any possibility for doubting that in the much smaller influence of the chemical state on the lines $K\alpha_3$, $K\alpha_4$ compared with the lines $K\alpha_1$, $K\alpha_2$ we are dealing with an essential difference in the behaviour of these lines, to the reason for which we shall come back in the following.

§ 2. *Discussion of the Results.*

Making use of Lindh's * measurements of the position of the K-absorption edge in sulphur and sulphates, the results

* Dissertation, Lund, 1923.

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of our measurements allow us to calculate the following values for the L_{II} and L_{III} levels expressed in the Rydberg frequency as unit for CuS and $CuSO_4$.

	Sulphide.	Sulphate.	Difference.
K (Lindh)...	181·85	182·68	0·83
L_{II}	11·96	12·70	0·74
L_{III}	11·87	12·62	0·75

In the first place it will be seen that the change in the levels is quite considerable, being for the K-levels about ½ per cent. and for the L-levels about 9 per cent. The theoretical interpretation of this change has to be sought in the changes of the binding of the electrons in the M-group. It is of interest, however, to point out that the changes are still small compared with the change to be expected if the behaviour of the sulphur atom in a sulphate compound could be simply compared with that of a six-fold charged sulphur atom.

In fact a simple estimate of the effect of the "outer screening"* to which the presence of the M-electrons in the neutral sulphur atom gives rise leads to a weakening influence on the binding of the K- and L-electrons which amounts to about one-half of the value of the L-levels themselves and thus is almost ten times larger than the difference in the levels observed in sulphur and sulphate. Even if for many purposes it is convenient to regard the sulphur atom in the sulphate molecule as a six-fold charged ion, it is thus clear that the presence of the electrons which in this picture are assigned to the oxygen atoms will exert a compensating influence on the energy necessary to remove an inner electron from the sulphur atom which is nearly as large as that exerted by the M-electrons in the neutral sulphur atom.

Compared with the shift of the levels, the shift of the emission lines themselves is very small, as is also to be expected from the theory, since the outer screening effect will be practically the same for a K-electron and an L-electron. As seen from the table, the experiments bring out that the K-level is changed slightly more than the L-levels. Considering, however, what we have just termed the compensation of the outer screening effect on the levels, it is hardly possible at present to offer any simple explanation of the small difference under consideration.

* Comp. Bohr. and Coster, *Zs. für Phys.* 1923.

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Due to the narrowness of the L-doublet, its change does not appear clearly from the table, but, as mentioned in the former section, the doublet is quite considerably affected by the chemical state, its width being 3·0 X.U. in sulphur and only 2·4 X.U. in sulphates. As regards the interpretation of this result, it must be emphasized that we do not at present possess any simple interpretation of the remarkable fact that the L-doublets are given with such close approximation by Sommerfeld's formula for the relativity influence of the binding of an electron moving round a point-charge. Compared with this formula, we may express our result by saying that the magnitude of this point-charge is almost a half unit larger for sulphur than for sulphates, or, in other words, that the so-called relativity screening constant is about 0·6 unit larger for sulphate than for sulphur. It is interesting to note that this change is of the same order of magnitude as the difference of the total inner screening responsible for the so-called screening doublet L_I L_{II} in the L-series. Not only the difficulties which at present stand in the way for a simple interpretation of the screening and the relativity doublets *, but also the difficulty of theoretically estimating the influence of the compensating effect referred to above seems to make any attempt of a closer interpretation illusory. At present it can only be a question of collecting material which perhaps will be of value for a future theory of the origin of the doublets. In this respect the observations in the present paper may give information of the same character as the observations of Siegbahn and Ray † as regards the anomalous behaviour of the K relativity doublet for the elements of the iron family, and also of the $L\alpha$-doublet ‡ for the palladium family and the rare earths. Although the latter result undoubtedly offers an interesting general confirmation of Bohr's explanation of the singular position of these families within the periodic table, no quantitative interpretation can at present be given.

Before concluding we may still draw attention to the difference in the behaviour of the lines $K\alpha_3$, $K\alpha_4$ compared to that of $K\alpha_1$, $K\alpha_2$ mentioned in the former section. This difference may be brought to an interesting connexion with the interpretation of the former lines advocated by Wentzel, according to which these lines originate from atoms in

* Compare Bohr and Coster (*l. c.*).

† *Ark. f. Mat. Astr. och Fys.* Bd. xviii. no. 14.

‡ Phil. Mag. Oct. 1924.

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which both K-electrons are removed. In fact, the increase in the charge of the sulphur atom accompanying this removal may be expected to have a large influence on the orbits of the looser-bound electrons in the neutral sulphur atom and in the sulphate molecule. In this respect the small shift in the lines under consideration might suggest that the ionization would produce an essential change in the constitution of the sulphate molecule to the effect of making the sulphur atoms behave similarly as in the isolated state. This may be connected with the fact that a sulphur atom which has lost both K-electrons may be able to bind 8 M-electrons with a considerable strength similar to that of the binding of the M-shell in the neutral argon atom. Due, however, to circumstances of the same kind as those playing a part in the effect discussed above, it would seem difficult to reach a simple theoretical interpretation.

§ 3. *Summary.*

The wave-lengths of the K-lines of a great number of sulphur compounds have been examined. It is found that the wave-lengths of the rays within the limits of experimental error are the same for sulphur and sulphide compounds on one hand and for sulphites and sulphates on the other, but that considerable differences are exhibited by the two classes of compounds, the lines $K\alpha_1$ and $K\alpha_2$ being shifted to shorter wave-lengths for the latter class at the same time as their distance apart is considerably diminished. For the lines $K\alpha_3$ and $K\alpha_4$ no such shift was observed. A general discussion as regards the theoretical interpretation of the results is given.

It gives me great pleasure to thank Professor N. Bohr for his many valuable suggestions during the whole course of the work. My thanks are also due to Mr. Y. Nishina for his unfailing friendly help and interest during the work, and to Professor G. Hevesy for kindly supplying me with the sulphur compounds for this investigation.

Universitetets Institut for teoretisk Fysik,
Copenhagen,
June 1925.

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LII. *Note on Production of Atomic Nitrogen and its Arc Spectrum.* By K. T. Compton, *Professor of Physics, Princeton University* *.

TWO years ago the writer, in collaboration with Dr. P. S. Olmstead †, succeeded in obtaining an atmosphere of atomic hydrogen at low pressure within a tungsten tube heated to about 2200° C., and measured the critical radiating potentials of atomic hydrogen by the method of electric impacts within this tube. This success led us to attempt a similar experiment in nitrogen. The possibility of thermally dissociating molecular nitrogen depends upon its heat of dissociation, which was then unknown, but was believed to be high. Langmuir ‡, for instance, states that practically every hydrogen molecule which strikes a hot tungsten filament is dissociated, whereas he could detect no evidence of such dissociation in the case of nitrogen at any temperature attainable with a tungsten filament, although he could have detected as much as 5 per cent. of dissociation. Nevertheless there was a chance that, within a high-temperature enclosure, a detectable degree of dissociation might be attained.

The results of two years of work on this problem have been entirely negative. We have succeeded, by the former method, in obtaining beautiful radiating potential curves of nitrogen (and also of carbon monoxide in several cases where the water-cooling of the apparatus was insufficient to keep cool a Khotinsky wax joint), but there was no evidence of any effect which could be ascribed to nitrogen in the atomic state.

Very recently Eucken § has shown that the heat of dissociation of N_2 into N is about 440 kg. cal. per mol. as compared with 90 in the case of hydrogen. This value is so high as to show the utter futility of further attempts along the lines mentioned above.

Another very different method of obtaining atomic nitrogen is suggested by the dissociation of hydrogen which is effected by collisions of the second kind with excited atoms of mercury, as described by Cario and Franck ‖, Duffendack and Compton ¶, and Turner **. This case illustrates a generalization which Franck †† added to the original theory of "collisions

* Communicated by the Author.
† Phys. Rev. xxii. p. 559 (1923).
‡ Journ. Am. Chem. Soc. xxxvi. p. 1708 (1914), xxxvii. p. 417 (1915).
§ *Ann. der Chemie*, 440, p. 111 (1924).
‖ *Zs. f. Phys.* xi. p. 161 (1922).
¶ Phys. Rev. xxiii. p. 583 (1924).
** Phys. Rev. xxiii. p. 464 (1924).
†† *Zs. f. Phys.* ix. p. 259 (1822).

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of the second kind" developed by Klein and Rosseland*. According to this theory, if any excited atom collides with a different atom or molecule, its energy of excitation may be transformed into kinetic, chemical, or excitation energy of the impacted molecule. The probability of thus effecting a chemical or excitation change seems to be the greatest if the energy of the original excited atom is just sufficient to effect the given change, and diminishes as the available energy more and more exceeds the necessary amount. The calculations of Turner indicate that practically every collision of an excited mercury atom with a hydrogen molecule results in its dissociation.

Now Eucken's value for the heat of dissociation of nitrogen corresponds to 19·05 in equivalent volts. There is no atom which is known to exist plentifully in an excited state of greater energy than this, under attainable laboratory conditions, except helium. This gas has been shown by numerous experiments to possess minimum excitation states of 19·73 and 20·56 volts energy, both existing in relatively large concentration in electrical discharges through helium at pressures of the order of 1 millimetre or more. Thus, if nitrogen were mixed with helium under conditions favourable for excitation of the helium, we should expect the nitrogen to be effectively dissociated by energy transferred from the excited helium atoms at collisions of the second kind.

Conditions favourable for this process may readily be predicted. To secure a large effect, a large electronic current through the gas is necessary. (It is well known that electrons are much more efficient agents for excitation and ionization than are positive ions.) In order to obtain large electron currents, ionization is necessary for neutralization of space charge around the cathode. If the gas-pressure is low, the necessary amount of ionization may occur by impact of electrons against normal helium atoms, since a sufficient number of electrons can, in the long free path, acquire energy exceeding the minimum ionizing energy corresponding to 24·5 volts. At higher gas-pressures, the chance of thus acquiring the ionizing energy is less, since a larger proportion of the electrons lose their energy by exciting helium atoms to the 19·7 and 20·5 volt states. In this condition, more of the ionization is of the cumulative or two-stage type, which becomes predominant at pressures above a few millimetres†. It can be shown‡, for instance, that an

* *Zs. f. Phys.* iv. p. 46 (1921).

† K. T. Compton, Phys. Rev. xx. p. 284 (1922); Phil. Mag. xliii. p. 531 (1922).

‡ K. T. Compton, Phys. Rev. xxii. p. 333 (1923).

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electron moving in a field of 50 volts /cm. through helium at 1 mm. pressure would make, on an average, three collisions after attaining the minimum exciting energy but before acquiring the minimum ionizing energy. If the gas-pressure were increased to 20 mm. the corresponding number of collisions would be 1200. These figures, combined with the fact that excitation is very probable and ionization very improbable at impacts by electrons whose energy only slightly exceeds the critical amount, illustrate the great importance of excited states and cumulative ionization at the higher helium pressures. Thus large current and high helium pressure are favourable to dissociation by action of excited helium atoms on nitrogen.

On the other hand, it is obvious that *low* partial pressure of nitrogen is necessary. If the nitrogen were present in too large proportion, the electrons would collide inelastically with nitrogen molecules, and thus lose their energy without effecting the excitation of the helium. This is, of course, the explanation of the fact that the spectrum of a helium discharge-tube containing a trace of foreign gas shows the lines of the foreign gas with greatly increased intensity. The helium atoms serve simply to increase, by elastic collisions, the total path of electrons through the tube, and thus increase the chance of collision with a molecule of foreign gas. It is only when the proportion of gas is extremely small that the electrons attain the energies required for excitation of the helium itself. Calculations similar to those above show that, as the helium pressure is increased, the amount of nitrogen must be diminished if most of the electrons are not to lose their energy directly to the nitrogen. At 20 mm. helium pressure, rough calculations show that the nitrogen pressure should be less than 0·01 mm., probably considerably less, in order to have most of the electron energy go directly into the helium. On the other hand, the amount of nitrogen must be sufficient to be appreciable.

These considerations suggest that there should be a rather limited range of conditions which are favourable, in a discharge-tube, to the production of atomic nitrogen in appreciable quantity by collisions of the second kind. If Eucken's value for the heat of dissociation is correct, helium should be the only gas capable of producing this association. Although the actual amount of nitrogen thus dissociated would of necessity be small, the *percentage* dissociation should be very high, since the chance of meeting of two nitrogen atoms would be much less than the chance of meeting with an excited helium atom, under the conditions postulated.

In this state of dissociation we should expect to find the

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spectrum of neutral atomic nitrogen strongly developed, owing to the favourable conditions for impact of electrons against the neutral atoms.

Since the appearance of Eucken's paper, the writer has been considering the possibilities outlined above, and was preparing to put them to an experimental test, when he read the very recent paper by Merton and Pilley * on "Experiments relating to the Spectrum of Nitrogen." These authors have, in a very elegant research, discovered that a new and distinct line spectrum of nitrogen is obtained only if the following conditions are fulfilled:—

(1) The nitrogen must be present in very small amount, mixed with helium at a pressure of about 30 mm.

(2) A condensed discharge (therefore large current density) must be used.

(3) The gases must be extremely pure, the slightest trace of impurities such as organic matter serving to bring out spectra of the impurities. (Only a trace of neon was present as an impurity.)

(4) If the nitrogen is too plentiful, the new line spectrum is replaced by the molecular band spectrum.

(5) If argon is substituted in place of helium, the new line spectrum is not obtained.

It is striking that every one of these conditions is exactly in line with the above considerations based on collisions of the second kind, and they were, in fact, predicted before the paper by Merton and Pilley appeared. The experimental work of these authors may therefore be considered as still another evidence of the importance of collisions of the second kind in the field of ionization and excitation.

The explanation of their experiment suggested by Merton and Pilley is, in effect, that the helium limits the electron velocities to about 20 volts, which may be the most favourable speed for exciting the nitrogen arc spectrum. Besides being less complete than the explanation suggested in the present paper, there is definite experimental evidence against it. In experiments both with two-electrode arcs and three-electrode tubes, in both of which the electron currents and speeds could be independently regulated over wide ranges, Duffendack † and Duffendack and Duncan ‡ have failed to find any evidence of line excitation at these voltages, and have not found any except spark lines to be excited at higher voltages. It is true that they probably had no appreciable proportion of atomic nitrogen present in their experiments. However, if the presence of sufficient atomic nitrogen could

* Proc. Roy. Soc. A, cvii. p. 411 (1925).

† Phys. Rev. xx. p. 665 (1922). ‡ Phys. Rev. xxiii. p. 295 (1924).

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be accounted for as the direct result of electron impacts, it is probable that they and others would have succeeded in exciting the new arc spectrum, as, for instance, the line spectrum of hydrogen may be excited.

The peculiarity of nitrogen appears to be, as pointed out by Merton and Pilley, that it dissociates under electron impacts into ions rather than atoms*. This, together with the well-proved fact that excitation is a much more prominent process than recombination in producing spectra†, accounts for the fact that ordinary excitation of nitrogen gives only the molecular band and the atomic spark spectra.

These considerations may be considered as supporting Eucken's value of the heat of dissociation of nitrogen. Had its value been as low as 280 kg. cal. per mol., we should have expected argon to be as effective as helium in the above experiment.

Finally, two extensions of this work suggest themselves. If neon should behave as does helium in bringing out the nitrogen arc spectrum, we may conclude that the heat of dissociation is as low as 370 kg. cal. per mol.; if it does not the value lies between this and 450, in agreement with Eucken. Thus spectroscopic observations may give some evidence regarding heats of dissociation. Furthermore, Eucken's value of 425 for the heat of dissociation of oxygen suggests that an arc spectrum of atomic oxygen might be obtained by similar experiments with this gas in helium. In this case, however, it is possible that the electron affinity of atomic oxygen may prevent its existence in the neutral atomic state in any considerable quantity. Likewise CO, with heat of dissociation 415, may give interesting spectra of C and O when properly mixed with helium. It seems possible that many spectroscopic peculiarities of mixtures of molecular with monatomic gases, such as the "comet-tail" spectrum, may find explanation of the sort suggested above.

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Note.—After this paper was written, the author found that Prof. M. N. Saha and Mr. N. K. Sur had previously suggested the desirability of investigating the action of excited helium on nitrogen, with especial reference to the possible production of the N line spectrum. It may be said, however, that the probable significance of the relation between the heat of dissociation of N_2 and the energy of excited helium was then unknown for lack of knowledge regarding the heat of dissociation. (See Phil. Mag. xlviii. p. 427, 1924.)

* Smyth, Proc. Roy. Soc. A, civ. p. 121 (1923).

† Compton, Turner, and McCurdy, Phys. Rev. xxiv. p. 597 (1924).

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LIII. *The Orientation of Crystals in Metal Test-Pieces subjected to Small Strains followed by Heat-Treatment.* By C. F. Elam, *M.A., Armourers and Brasiers Research Fellow* *.

In the following paper a comparison has been made of the orientations of crystals of aluminium, an aluminium-zinc alloy containing 18 per cent. zinc, and iron which have been formed by the method of straining followed by heat-treatment, with the object of ascertaining whether the method of manufacture influenced the orientation. It is known from the work of Polanyi † and others that, with severe cold work such as occurs in wire-drawing, the crystals tend to assume certain definite positions relative to the direction of stress, and Glöcker ‡ has shown recently that on annealing such material this orientation is not completely obliterated. Edwards and Pfeil §, in describing their tests on iron crystals, were of the opinion that there was a similarity in the orientation, and concluded that the small crystals in the aggregate which eventually grew were so related to the axis of pull that they underwent a type of deformation which favoured crystal growth. The question as to whether the large crystals were formed from new crystal nuclei, *i.e.* by a process of recrystallization or from some of the original small crystals, was discussed by Professor Carpenter ‖ and the author in a previous paper. A similarity of orientation would favour the latter view rather than the former.

Altogether the axes of sixty-four crystals have been determined and compared. The majority of the pure aluminium crystals determined were those occupying the whole parallel po tion of a test-piece, but in one case all the crystals in a test-piece containing four were determined. In the case of iron, the axes of six crystals in one strip, kindly sent to the writer by Professor C. A. Edwards, were determined by Mr. R. L. Aston in the Cavendish Laboratory, Cambridge, who has kindly allowed his results to be included, in addition to other crystal axes determined by the writer. Of the alloy crystals, all were turned out of bars consisting of several crystals.

The method of determining the crystal axes in a test-piece has already been described ¶. It is unnecessary to give the actual figures, as these in themselves do not show clearly how

* Communicated by the Author.

† Ettisch, Polanyi, and Weissenberg, *Zeit. für Physik*, iv. & vii. 1921, etc.

‡ Glöcker, *Zeit. für Physik*, xxxi. (1925).

§ Edwards and Pfeil, Journ. Iron & Steel Inst. 1924, no. 1.

‖ Carpenter and Elam, Proc. Roy. Soc. A, c. (1921).

¶ Müller, Proc. Roy. Soc. A, cv. (1924).

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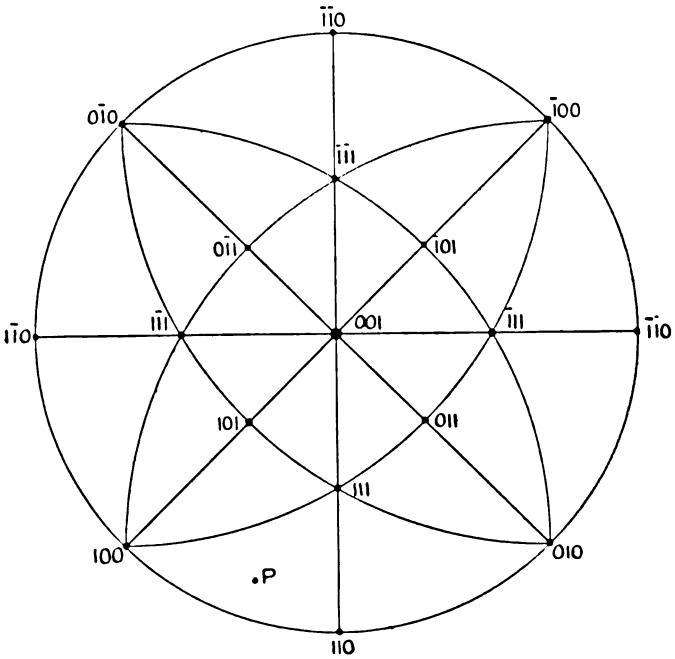
the crystals vary in relation to the axis of the test-piece. For this purpose the stereographic projection of the crystal axes was made in which one of the cubic (100) axes was in the centre of the figure, and the four octahedral (111) axes were arranged symmetrically round it * (fig. 1). In order to fit the crystal axes determined by X-rays on to this figure, it is necessary to rotate them (using a stereographic net) until one of the cubic (100) axes coincides with the centre of the diagram. The axis of the text-piece is then represented by a point P lying in one of the twenty-four spherical triangles in the figure. These triangles are all similar, and by choosing

Fig. 1.



a suitable cubic axis to put in the centre of the figure, the axes of all the test-pieces can be made to fall into one particular triangle, when their relative positions can be more easily compared. Figs. 2, 3, 4, and 5 each represent one of these triangles, in which the positions of the axes of the test-pieces have been marked. It will be at once apparent that a great variety of orientation is met with, although in the case of aluminium most of the crystals favour a position near the (110) axis, and none have yet been obtained near a (100) axis. Several of the alloy and

* Taylor and Elam, Proc. Roy. Soc. A, cviii. (1925).

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Fig. 2.—Pure aluminium.

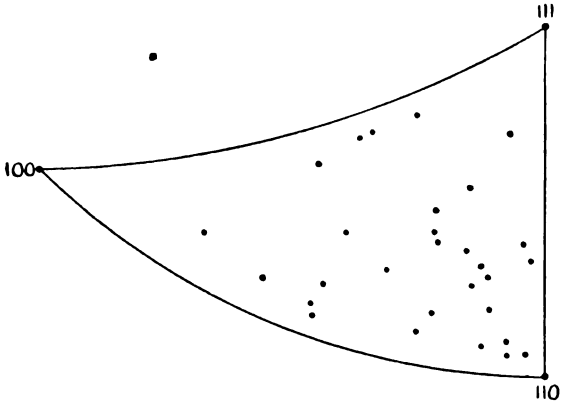


Fig. 3.—Aluminium test-piece consisting of four crystals.

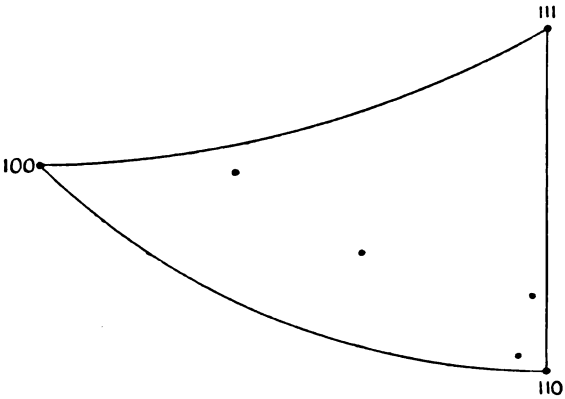
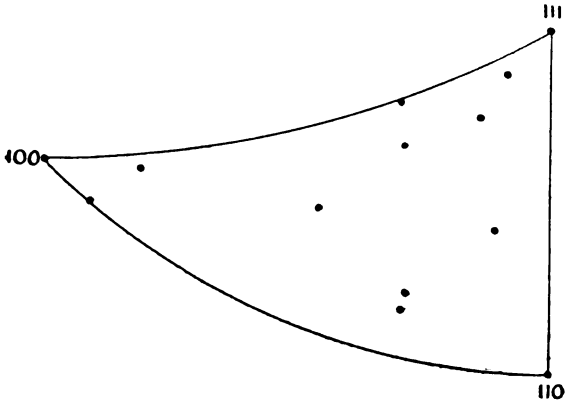


Fig. 4.—Iron.



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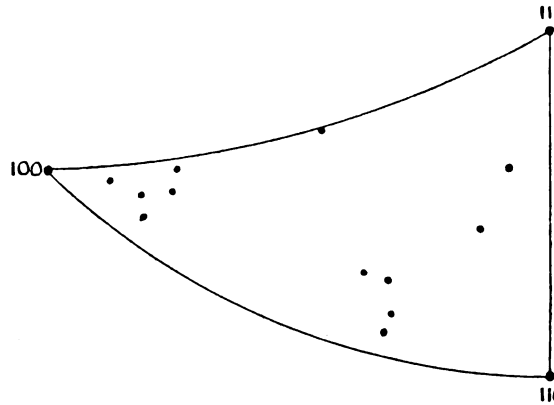
iron crystals, however, were near this position. It is possible that the rate of growth is more rapid in some directions than others, so that the majority of the largest

Fig. 5.—Aluminium-zinc alloy.



crystals produced may favour one orientation. This question could only be decided after an examination of a large number of crystals of varying sizes. As has been pointed out, all test-pieces in fig. 2 were single-crystal test-pieces, but those in the other diagrams represent considerable variations in size, and there appears to be no relation between crystals in the same test-piece. Furthermore, some experiments described by Professor Carpenter and the writer * showed that the orientation of a crystal could be changed by straining and heat-treating, and that the new orientation appeared to have no relation to that of the original crystal. The process is the same as that of converting an aggregate of small crystals into one crystal. It is not, however, possible to say how this re-orientation takes place.

Summary.

The results of the determination of the crystal axes of sixty-four crystals produced by a process of straining followed by heat-treatment show that the variety of orientation is great, although it is possible that some directions are more favoured than others. The direction of straining does not influence the orientation of the crystals to the extent that was expected.

Royal School of Mines,
June 15th, 1925.

* Carpenter and Elam, Proc. Roy. Soc. A, cvii. (1925).

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LIV. *The Heating Effect of the γ-Rays of Radium B and Radium C.* By C. D. Ellis, *Ph.D., Fellow and Lecturer in Trinity College, Cambridge, and* W. A. Wooster, *B.A., Hugo de Balsham Student and J. M. Dodds Student of Peterhouse, Cambridge* *.

Introduction.

In this paper we describe measurements of the heating effects of the γ-rays of radium B and radium C. The main difficulty was to find a method of measuring the γ-ray heating separately and not superimposed on the very much greater α-particle heating effect of radium C. This was accomplished in the present experiments by means of an automatic compensation of the α-particle heating.

It is the object of this introduction to point out that this measurement has an importance beyond that of determining the fraction of the disintegration energy emitted as γ-rays, since, combined with other measurements, it leads to a knowledge of the absolute intensities of the different γ-rays.

It is generally accepted that the quantum dynamics apply to the nucleus and that the emission of γ-rays consists in the emission of discrete quanta $h\nu_1$, $h\nu_2$, ... so that the relative intensities of the different γ-rays must mean the relative number of quanta emitted. But this discrete emission accompanies the disintegration of the nucleus, itself a discrete phenomenon, making it possible in this case to speak of the absolute intensities in the sense of the probabilities p_1, p_2, ... that any one disintegration will be accompanied by the emission of one quantum of frequency ν_1, ν_2 .... It is unnecessary to stress the importance of knowing these probabilities, they describe the entire phenomenon of emission and would lead to an immediate interpretation of the sets of nuclear stationary states which are responsible for the emission of the γ-rays.

These probabilities can only be found by a combination of three different measurements, namely, the heating effect of the γ-rays, the relative intensities of the β-ray lines, and the coefficient of internal conversion of the γ-rays in the parent atom. To see this we must consider the γ-ray emission in more detail. When an atom disintegrates with emission of a quantum of frequency ν, then in the majority of cases this quantum escapes from the atom, but there is a certain probability α that it will be converted inside the

* Communicated by Prof. Sir E. Rutherford, F.R.S.

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parent atom and give rise to a fast electron. This probability of internal conversion was discussed by Ellis and Skinner (Proc. Roy. Soc. A, cv. p. 186, 1924), who showed that in a typical case of radium B it must be greater than one-tenth, and Gray ('Nature,' Jan. 3rd, 1925) found even greater values for radium D. The natural β-ray spectra are due to this internal conversion, and we may express the relative intensities (*i. e.*, number of electrons) of the different β-ray lines in the general form

$$\frac{I_1}{I_2}=\frac{p_1\alpha_1}{p_2\alpha_2};\quad \frac{I_1}{I_3}=\frac{p_1\alpha_1}{p_3\alpha_3},\text{ etc.}$$

This statement must be extended to cover the fact that the γ-ray may be converted in any of the electronic levels, so we define the appropriate coefficients ${}_1\alpha_K$, ${}_1\alpha_{L_I}$, ${}_1\alpha_{L_{II}}$, ... ${}_1\alpha_{M_V}$ .... etc., and the intensities of the corresponding β-ray lines are in the ratio of these quantities when multiplied by the p's. These relative intensities can be found directly from the β-ray spectra, and form one stage in the determination of the p's. The next stage is to find the α's, the probabilities of internal conversion. There are different methods of doing this which will not be entered into here; instead we turn to the last measurement by which these relative intensities can be turned into absolute ones. For this purpose it is necessary to find the total energy E emitted per sec. in the form of γ-rays by a known quantity of radioactive material. Suppose the quantity is such that n atoms are disintegrating per sec., then

$$E=n\{h\nu_1 \cdot p_1[(1-{}_1\alpha_K)(1-{}_1\alpha_{L_I})(1-{}_1\alpha_{L_{II}})\ldots]+h\nu_2 \cdot p_2[\ldots\}.$$

This quantity E is of course the heating effect of the γ-rays, measurements of which are described in this paper, and it is at once seen how essential a position it occupies in the problem of the absolute intensities.

There is an alternative measurement which can take the place of the heating effect, and that is to determine the total number, Q, of γ-rays emitted. This could be represented as

$$Q=n\{p_1[(1-{}_1\alpha_K)(1-{}_1\alpha_{L_I})\ldots]+p_2[\ldots\}.$$

Kovarik * has recently carried out this experiment, and reference will be made later to his results which are in substantial agreement with ours. Experiments to determine the relative intensities of the γ-rays are in progress.

* Kovarik, Phys. Rev. v. p. 559 (1924).

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General Considerations.

During the course of their work on the heating effect of the α-rays of radium C, Rutherford and Robinson * found it necessary to make experiments to determine the order of magnitude of the heating effect of the γ-rays, which are also emitted by radium C. Their method was to measure first the effect due to the α-rays, the γ-rays being allowed to escape, and then to absorb a certain fraction of the γ-rays by means of lead screens and find the increase in the total effect. These experiments were difficult to carry out, but still it was possible to show that the γ-ray heating effect must be about 7 per cent. of the total and that under practical conditions of incomplete absorption of the γ-rays a maximum increase of only 4 per cent. was to be expected when the lead screens were added. These figures bring out clearly the impossibility of obtaining any accuracy by a subtraction method; in fact, to obtain a final 5 per cent. accuracy in the γ-ray heating it would be necessary to carry out both the main measurements with an accuracy of about 1 in 500. It is very difficult to obtain such an accuracy in this type of experiment, and so the only other alternative was adopted, that of finding a method by which the γ-ray heating could be measured independently of that of the α-rays. The general principle is not difficult to find since the α-rays are easily absorbed whereas the γ-rays are penetrating, so that if an absorber, such as a block of lead, were placed some distance from the source the only heating effect in it would be due to the γ-rays. In practice, however, the matter is not so simple, as the following figures show. Suppose a small tube containing 100 millicuries of radium emanation is taken as a source. The total γ-ray energy emitted by the disintegration products radium B and C is about 0·8 calorie an hour, and even with the lead block placed only 6 mm. from the source it is not practicable to absorb more than 1/8 of the γ-rays, giving a heating effect of 0·10 calorie an hour. But the heating effect of the α-rays from the emanation, radium A, and radium C is over 10 calories an hour, and even if the α-rays are prevented from leaving the immediate neighbourhood of the source, the problem still remains of measuring a very small heating effect of 1/10 calorie an hour in the presence of a source generating heat at a rate 100 times as great. Various methods of shielding were tried but they were not successful, the heat radiated from the source always being in excess of that produced by

* Rutherford and Robinson, Phil. Mag. [6] xxv. p. 312 (1913).

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the γ-rays. We therefore adopted a slightly different principle which finally proved quite successful. Instead of trying to remove the α-particle heating we arranged for an automatic compensation of its effect.

Apparatus.

The actual calorimeter consisted of a hollow circular cylinder made out of four equal sectors, and is shown diagrammatically in fig. 1. Two opposing ones A and B were respectively of lead and aluminium, and they were insulated from one another by the two other sectors C and D of Balsa wood. The aluminium sector had holes bored in it so as to make it have the same heat capacity as the lead sector. This composite cylinder was fixed inside another closely fitting cylinder of Balsa wood and caps of Balsa wood placed at each end. The whole fitted inside a thick copper case. Nineteen silver-constantan thermocouples in series were wound round the composite cylinder so as to record any temperature difference of the lead and aluminium sectors. Through the centre hole of the composite cylinder ran an 8 mm. copper rod, bored throughout its length with a 3 mm. hole. This rod was supported at its two ends by the outer copper case and did not touch any portion of the composite cylinder, there being a three millimetre clearance. The radioactive source, which was a small glass tube 8 mm. long filled with radium emanation, was placed in the centre hole of the copper rod. This arrangement provided an automatic compensation of the heat emission due to the α-particles, for although the central copper rod became heated, just as much heat was received from it by the aluminium sector as by the lead sector. Since these were of equal heat capacity their temperature rose by the same amount, and the galvanometer connected to the thermocouples showed no deflexion. This compensation will also hold for β-rays, since radium B and C appear to emit few if any electrons faster than 12,000 $H\rho$, and Varder's* results show that even these are almost completely absorbed in the copper tube of 2·5 mm. thickness. The same would be true for any radiation which escaped from the copper tube but which was yet completely absorbed in the aluminium sector and hence also in the lead one. As soon, however, as the radiation is sufficiently penetrating to pass through the aluminium without being completely absorbed, as in the case of the γ-rays, then a temperature

* Varder, Phil. Mag. xxix. p. 725 (1915).

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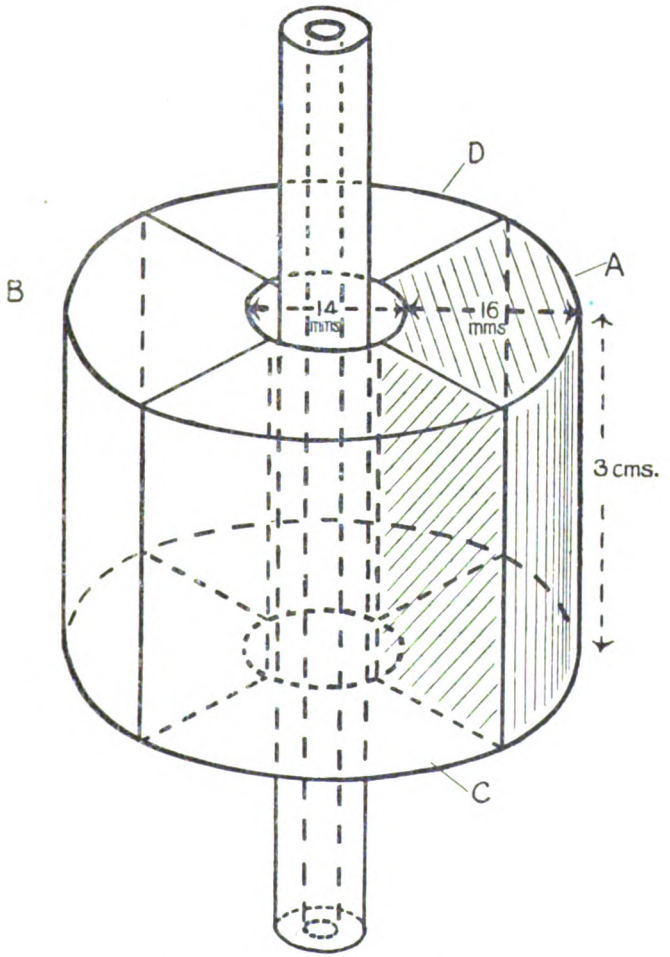
difference will be set up because the radiation will have been more absorbed in the lead and therefore have given up more heat to it. Hence, although the lead and aluminium sectors receive far more heat by radiation from the central

Fig. 1.



copper tube than they do by absorption of the γ-rays, the deflexion of the galvanometer, which measures the difference of temperature of the sectors, depends only on the γ-ray energy absorbed. With this arrangement the large α-particle heating can be made almost to cancel out, and

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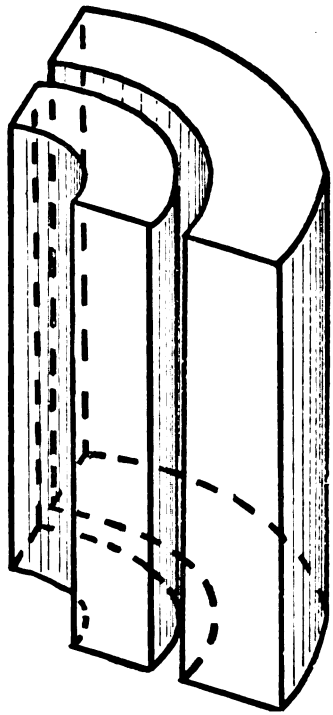
except for the necessity of rather more complicated calibration experiments with heating coils, the γ-ray heating effect could be obtained with the same ease as the total heating effect of a radioactive body.

Certain further details of the apparatus can conveniently be given at this point. Each of the metal sectors consisted of an inner and outer part as shown in fig. 2, and the

Fig. 2.



thermocouples were wound round the outer face of the inner part. In this way they registered the temperature of the centre of the metal blocks. The thermocouples were made by Wilson's method * by taking a long piece of constantan wire and silvering alternate sections, and were connected to a moving coil galvanometer of 24 ohms resistance giving 220 mm. scale deflexion at 1 metre for 10^{-6} ampere. Owing to the smallness of the main effects slight thermoelectric effects in the galvanometer became very troublesome,

* Wilson & Epps, Phys. Soc. Proc. xxxii. p. 326 (1920).

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but this difficulty was overcome by placing a reversing key close to the apparatus and taking as reading the difference of the deflexions with the key in its two positions. This reversing key was especially designed to avoid thermo-electric effects inside itself.

Heating coils were sunk in the lead and aluminium sectors for calibration purposes, and the currents in them measured on calibrated direct-reading instruments. In the case of the lead two heating coils were used, one in both the inner and outer sectors, making it possible to study the effects of different distributions of heat production.

Experimental Results.

The method of making measurements was to observe the maximum deflexion reached when the rate of heat supply was equal to the rate of heat loss. It was a disadvantage of this apparatus that it required forty-five minutes to reach this point, but the necessity for having a large mass of lead to absorb a considerable fraction of the γ-rays made it undesirable to shorten it. It was intended to employ for the final measurement a sensitive Paschen galvanometer, since the galvanometer we used for the preliminary experiments gave only 7 mm. deflexion. This small deflexion was measured by means of a travelling microscope, and the error involved was found to be less than 1 per cent. Since this error was less than the others involved in the experiment, we did not consider it necessary to use the more sensitive instrument. The actual rise curve was rather complicated, a maximum deflexion being reached in 45 minutes, after which the deflexion decreased slowly. The initial rise was approximately an exponential with a half period of 8 minutes, but if after the maximum had been reached the source of heat was taken away, there was a sharp initial fall and then a slow return with a half period of about three hours. The explanation of this behaviour lies in the fact that the galvanometer only measures the difference of temperature of the lead and aluminium, and that the temperature-time curves of the lead and aluminium sectors considered separately are somewhat complicated owing to there being heat transfer not only from the heated metals to the colder surroundings but also from the lead to the aluminium. It was not thought necessary to investigate this in more detail, it being sufficient to make the calibration measurements under exactly the same conditions as the γ-ray experiments and to verify, as we did, that the

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deflexion-time curves were identical in the two cases. Readings of the deflexion were taken every two minutes over a period of an hour, and the maximum deflexion taken as the mean of the six measurements made between 40 and 50 minutes from the start.

The results for the γ-ray heating were very concordant, and are shown in Table I. The first column shows the amount of radioactive material, the second the deflexion, and the third column the values of these deflexions when increased to correspond to a source of 70·5 mg.* The origin of this particular value will become clear when we consider the calibration measurements. It can be seen that the values in column 3 agree closely, and we can take the value 6·81 mm. for the deflexion for 70·5 mg. as being correct to about 1 per cent.

TABLE I.

Value of source in millicuries.	Deflexion in mm.	Deflexion for 70·5 millicuries.
58·02	5·60	6·81
48·45	4·69	6·83
40·47	3·81	6·64
33·80	3·31	6·90
28·23	2·75	6·87
	Mean	6·81

The whole of this deflexion cannot be attributed to γ-rays, that would only be the case if the compensation of the α-particle heating were exact. This point was investigated by putting a small heating coil in place of the emanation tube and generating heat there to correspond to the α's of about 100 mg. A deflexion of 0·8 mm. was found to result, showing that with this arrangement the disturbing effect of the α-rays was reduced to one-tenth of that of the γ-rays. This small residual effect can easily be corrected for, since the amount of the α-particle heating is known to 1 in 200. We obtained this correction at the same time as the general calibration in the following way. The small heating coil already referred to was placed in the central copper tube,

* We are greatly indebted to Mr. L. Bastings for determinations of the strength of the sources used in these experiments.

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and in all the calibration experiments the same constant current sent through it so as to give a heating effect equal to that of the α's and β's from 70·5 mg. Various currents were then sent through the heaters in the lead block, and also the sector in the aluminium block. The result of many experiments, using either the lead or aluminium heater alone, or both combined, was that the resulting deflexion δ mm. was connected by the following equation with the heat C_{Pb} produced in the lead block, and that C_{Al} produced in the aluminium

$$\delta = 0{\cdot}421C_{Pb} - 0{\cdot}573C_{Al} + 0{\cdot}57,$$

where C_{Pb} and C_{Al} are expressed in units of 10^{-6} cal. per sec. It may be mentioned in passing that the term 0·57 represents the residual effect of the α's from 70·5 mg. The inequality of the coefficients of C_{Pb} and C_{Al} is due to different conditions of heat loss of the two sectors.

This calibration equation is valid for C_{Al} varying between 1/11 and 1/3 that of C_{Pb}, and with γ-rays the heat produced in the aluminium is about 1/7 of that produced in the lead. It was important to investigate whether the value of the deflexion depended on the distribution of the heat production, for with the γ-rays the heat is produced throughout the body of the lead, the distribution being unequal due to absorption, whilst in the calibration experiments the heat comes from the two small heaters. It seems unlikely that any error was introduced here because the deflexion did not change when the ratio of the amount of heat produced in the inner lead heater to that in the outer varied between the limits 6 and 1·7. It was also possible that the heat conducted down the wires leading from the heaters might introduce errors, since in the γ-ray case the heaters, if anything, are at a lower temperature than the lead, whereas in the calibration experiments they are at a higher one. However, no change was produced on increasing the conductivity of the leads by a factor of 30, so any correction for this effect is unnecessary to our accuracy. Viewing the calibration experiments as a whole, we consider a reasonable estimate of the error involved to be 3 per cent.

Calculation of Results.

(a) *Amount of γ-rays absorbed.*

Before the deflexion obtained with a known source of γ-rays can be combined with the calibration equation to give the total γ-ray energy, it is necessary to calculate the fractions absorbed in the lead and aluminium sectors. For

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this purpose we require the coefficient of true energy absorption as distinct from the scattering, *i.e.* deflexion of energy, and to be applicable to the present experiment it must have been determined over a range of 16 mm. of lead after passing through a preliminary filter of 2·5 mm. of copper. We are greatly indebted to Mr. Ahmad for measuring the total absorption coefficient under precisely these conditions. He found the value $2{\cdot}64 \times 10^{-23}$ for the atomic coefficient. This may be represented as the sum of three coefficients

$$(\tau + r + \sigma) = 2{\cdot}64 \times 10^{-23},$$

where τ, r, and σ represent respectively the photoelectric absorption, the energy absorption in the scattering process, and true scattering. The value of the total energy absorption coefficient $(\tau + r)_{Pb}$ may be found in the following manner, as suggested by Mr. Ahmad. For aluminium his measurements give the total atomic absorption coefficient as $0{\cdot}278 \times 10^{-23}$, but in this case τ is negligible, and so

$$(r + \sigma)_{Al} = 0{\cdot}278 \times 10^{-23}.$$

Now the coefficients r and σ are both known to vary linearly with N, the atomic number, hence

$$(r + \sigma)_{Pb} = \frac{82}{13}(r + \sigma)_{Al} = 1{\cdot}757 \times 10^{-23},$$

giving

$$\tau_{Pb} = 0{\cdot}883 \times 10^{-23}.$$

It now remains to find r_{Pb}, and this may be done by deducing from the mean X-ray result

$$\tau = 2{\cdot}29 \times 10^{-2} \lambda^3 N^4$$

the "effective" wave-length $\lambda = 0{\cdot}0205$ Å.U. Using this value, r_{Pb} can now be calculated by means of the formula

$$r = \sigma_0 N \frac{\alpha}{(1 + 2\alpha)^2},$$

$$\sigma_0 = 6{\cdot}65 \times 10^{-25}, \qquad \alpha = \frac{0{\cdot}0242}{\lambda},$$

proposed by Compton, and strongly supported by the experiments of Owen * and of Ahmad †. The result is

$$r_{Pb} = 0{\cdot}570 \times 10^{-23},$$

giving as total atomic coefficient of energy absorption for the above conditions

$$(0{\cdot}883 + 0{\cdot}570) \times 10^{-23} = 1{\cdot}453 \times 10^{-23}.$$

* Owen, Phys. Soc. Proc. xxxvi. p. 355 (1924).
† Ahmad, Proc. Roy. Soc. A. cv. (1924).

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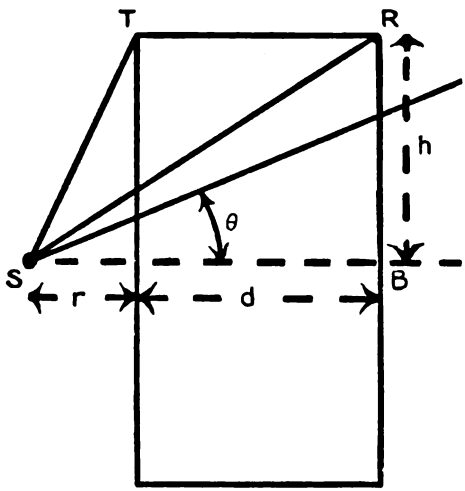
The corresponding ordinary coefficient k is 0·482 cm.$^{-1}$, this coefficient consisting of 0·293 for the photoelectric absorption and 0·189 for energy absorption in the scattering process. The value for aluminium is less important and comes to 0·058 cm.$^{-1}$, when deduced from the above equations. It may be noted that this calculation does not depend on any particular picture of the scattering process, but merely on the validity of Compton's results used as interpolation formulæ. However, in view of the rather indirect method by which these values were obtained, it was thought best to carry out the further calculations with coefficients $0{\cdot}482+\delta\tau$ and $0{\cdot}058+\delta\tau'$, and to express our final result with a correcting factor involving first and second order terms in $\delta\tau$ and $\delta\tau'$. Should later work lead to slightly different values of the absorption coefficients, our experimental result can be recalculated at once by means of this factor.

Fig. 3.



The calculation was carried out first with the approximation of the source being considered as a point half-way along the axis of the cylinder, and remembering that each sector formed one quarter of the cylinder, the fraction absorbed can be written

$$\frac{1}{4}\left[\int_0^{RSB} f(\theta)\left(1-e^{-\frac{kd}{\cos\theta}}\right)\cos\theta\,.\,d\theta + \int_{RSB}^{TSB} f(\theta)\left(1-e^{-k\left(\frac{h}{\sin\theta}-\frac{r}{\cos\theta}\right)}\right)\cos\theta\,.\,d\theta\right],$$

where the symbols have the meaning shown in fig. 3.

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The term $f(\theta)$ represents the initial transmission factor of the copper tube, and is included in the integrals since it is a function of θ owing to the varying thicknesses of copper traversed by the oblique rays.

The actual calculation was a little more complicated in order to take into account the gaps between the inner and outer sectors. Further, the fact was allowed for that the absorption coefficient 0·482 cm.$^{-1}$ represents a mean value for passage through a thickness of 16 mm. at various obliquities. Assuming this value corresponded exactly to passage at 20°, small corrections were applied to give an appropriate k for every θ. After this further small corrections were applied, making in all -3 per cent., to take into account the finite length of the source, the holes bored out to contain the heaters, and the escape of electrons from the surface of the lead. It might be thought that errors would arise from the escape of the lead K radiation excited by the absorption of the γ-rays, since only the L absorption is here effective, but a short calculation shows that this correction is negligible.

The final result of the calculation can be expressed in this way. If h_γ calories per sec. be emitted by the radioactive source, then the amount absorbed in the lead and aluminium sectors is respectively $A_{Pb}h_\gamma$ and A_{Al}, h_γ, where

$$A_{Pb} = (23{\cdot}44 + 32{\cdot}9\delta\tau - 26(\delta\tau)^2)\frac{\pi}{4}\cdot\frac{1}{180},$$

$$A_{Al} = (2{\cdot}38 + 44{\cdot}1\delta\tau')\frac{\pi}{4}\cdot\frac{1}{180}.$$

(b) *Deduction of Heating Effect.*

We can now combine the three stages, the deflexion due to 70·5 mg., *i. e.* 6·81 mm., the calibration equation, and the fractions absorbed A_{Pb} and A_{Al}. If H_γ represents the γ-ray energy in 10^{-6} calorie per sec. emitted by 70·5 mg., then in the calibration equation

$$\delta = 0{\cdot}421\,C_{Pb} - 0{\cdot}573C_{Al} + 0{\cdot}57$$

we have to substitute

$$C_{Pb} = H_\gamma\,.\,A_{Pb}, \qquad C_{Al} = H_\gamma\,.\,A_{Al}.$$

From H_γ we then obtain the γ-ray energy $\mathbf{H}_\gamma$ emitted by 1 gram of radium in equilibrium, in calories per hour

$$\mathbf{H}_\gamma = \frac{8{\cdot}62}{1 + 1{\cdot}63\delta\tau - 1{\cdot}3(\delta\tau)^2 - 3{\cdot}0\delta\tau'}.$$

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Dropping the correcting terms for possible subsequent changes in the value of the absorption coefficients, we have:

> *The amount of radium* B *and radium* C *that is in equilibrium with* 1 *gram of radium emits* **8·6** *calories per hour in the form of γ-rays.*

We estimate this result to be correct to 5 per cent.*, and we have therefore made no correction for the transient equilibrium of the products in the emanation tube.

Division of the Energy between Radium B *and Radium* C.

It is important to find how this total heating effect is to be divided between radium B and radium C. A simple method of doing this is based on a knowledge of the apparent absorption coefficients of the total radium B rays, of the total radium C rays, and of the combined rays.

Suppose E_B, E_C are the γ-ray energies emitted by the amounts of radium and radium C in equilibrium with a certain quantity of radium, and E_{BC} represents the total γ-ray energy emitted by the two bodies. If μ_B and μ_C are the respective energy absorption coefficients of the corresponding γ-rays for any thickness d, then

$$E_B + E_C = E_{BC},$$
$$E_B e^{-\mu_B d} + E_C e^{-\mu_C d} = E_{BC} e^{-\mu_{BC} d}.$$

If we write

$$p = E_B/E_C,$$

then

$$p = \frac{e^{-\mu_C d} - e^{-\mu_{BC} d}}{e^{-\mu_{BC} d} - e^{-\mu_B d}}.$$

There are no measurements of these absorption coefficients available which have been made under precisely the required conditions, but a preliminary estimate may be made as follows. The one quantity we know is $\mu_{BC} = 0{\cdot}482$, and the conditions to which it refers are preliminary filtering through 2·5 mm. copper and then absorption determined over 16 mm. of lead. If we use this value, then p must be taken to mean the ratio E_B/E_C after passing the filter. The value assigned to μ_B is of little importance, since $e^{-\mu_B d}$ is very small over this large thickness, but a value $\mu_B = 2{\cdot}42$ may be used, calculated by the usual formulæ from the mean wave-length

* A preliminary account of this work was published in Camb. Phil. Soc. xxii. 1925, in which the value 8·1 cals./hour was given. The difference represents the result of the more detailed calculation of the absorption given here.

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of the radium B γ-rays. The really important quantity is μ_C. There is no essential difficulty in measuring it under these conditions, but since it has not yet been done we must take Ahmad's* values for the absorption coefficient of the total radium B and C radiation after filtering through 1 cm. of lead. His value was 0·426, and since the 1 cm. filter will have removed all but about 2 per cent. of the radium B rays, we may take this value as μ_C. These three values $\mu_{BC} = 0{\cdot}482$, $\mu_C = 0{\cdot}426$, $\mu_B = 2{\cdot}42$, referring to $d = 1{\cdot}6$ cm., give $p = 0{\cdot}10$.

If we were to consider the value $\mu_C = 0{\cdot}426$ too high and take instead $\mu_C = 0{\cdot}42$, we should obtain $p = 0{\cdot}11$. Moseley and Robinson †, by comparing the number of ions formed in air by the softer and harder radiations of radium B and C, deduced a ratio $p = 0{\cdot}074$, while a similar measurement by Miss J. Szmidt ‡ gave $p = 0{\cdot}072$. There seems, then, little doubt about the general order of magnitude, but we believe the value $p = 0{\cdot}10$ to be nearer the truth, since the method of calculation employed by the above authors would have tended, even more than the one used here, to attribute part of the harder radium B radiation to radium C. This conclusion receives further support from the work of Moseley and Makower §, who found that 12 per cent. of the ionization given by radium B and C, after passing through 3 mm. of lead, was to be attributed to radium B. It must be remembered that this value of p refers to the ratio after passing 2·5 mm. of copper, and so needs a correction since the radium B rays are more absorbed in the copper than those of radium C. This correction proves to be only +3 per cent., and in view of the other uncertainties may be neglected. More work is required on this important point, but accepting the above provisional value we obtain the following heating effects for radium B and radium C separately. These are also expressed in terms of volts per atom disintegrating, the values being obtained on the basis of Geiger's ‖ recent value for the number of α-particles emitted by 1 gram of radium, *i.e.* $3{\cdot}4 \times 10^{10}$.

Heating Effects of Radium B and Radium C.

	cals./hour.	volts/atom.
Radium B	0·86	$1{\cdot}85 \times 10^5$
Radium C	7·7	$16{\cdot}6 \times 10^5$

* *Loc. cit.*
† Phil. Mag. [6] xxv. p. 312 (1913).
‡ Phil. Mag. [6] xxviii. p. 527 (1914).
§ Phil. Mag. [6] xxiii. p. 302 (1912).
‖ Geiger and Werner, *Zeit. für Phys.* xxi. p. 197 (1924).

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Discussion.

It was pointed out in the introduction that the full use of a value for the heating effect of the γ-rays could only be made in conjunction with certain other measurements, but it is useful at this stage to effect a comparison with previous determinations and to see in a general way to what extent our measurement fits in with existing views.

Our result 8·6 calories an hour is in approximate agreement with that obtained in 1914 by Rutherford and Robinson, 6·7 calories an hour; but a closer comparison is hardly justified, since the earlier measurement aimed only at settling the order of magnitude. Reference has already been made to the experiments of Kovarik, where he determined the total number of quanta of all frequencies emitted by a known quantity of radium B and C. His results are not directly comparable with ours at this stage, since the two measurements are connected by means of the relative intensities of the β-rays, and accurate measurements on this point have yet to be made. Still, it is easy to see that our measurement of the heating effect is in general agreement with his conclusion that on the average two γ-rays are emitted for every two disintegrations, one of radium B and one of radium C. For we may deduce from the work on β-ray spectra that the mean energy of the radium B γ-rays is $0{\cdot}3 \times 10^6$ volts, and that of the radium C γ-rays is between 1·1 and $1{\cdot}7 \times 10^6$ volts, whereas we found a total energy emission from the two bodies of $1{\cdot}85 \times 10^6$ volts, which could be accounted for on the basis of one γ-ray from each body. However, we do not wish to draw any detailed conclusions until the measurements on the relative intensities of the β-rays and their internal absorption coefficients have been made.

There is one further point which may be mentioned. It has been suggested by one of us that the emission of γ-rays is due to transition between a set of stationary states in the nucleus, the latter either being left in an excited state as the result of the previous disintegration, or being put into such a state by its own disintegration. In either case this view of only one excitation, coupled with the detailed picture of the stationary states that have been given, would preclude the emission of a large number of quanta at each disintegration and would suggest rather a number close to one, in agreement with the results of Kovarik's and our experiments.

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SUMMARY.

(1) The heating effect of the total γ-rays emitted by the quantity of radium B and radium C in equilibrium with 1 gram of radium has been found to be 8·6 calories an hour.

(2) Of this 0·86 calories an hour is to be attributed to radium B and 7·7 calories an hour to radium C.

(3) The importance of determining the absolute intensities of the γ-rays is pointed out, and it is shown that a knowledge of the heating effect is an essential step in the process.

We would like to thank Professor Sir Ernest Rutherford for his continual help and advice during the course of the experiments. We are indebted to Mr. G. R. Crowe for the preparation of the emanation tubes.

LV. *The Motions of Electrons in Oxygen.*

By H. L. BROSE, *M.A., D.Phil., Christ Church, Oxford* *.

1. IN the accounts of previous researches on the motion of electrons in gases which have been made in the Electrical Laboratory, Oxford, a method has been described of determining the velocity W in the direction of a uniform electric force and the velocity of agitation U of electrons in gases. The investigations of the motion of electrons in nitrogen, hydrogen, and oxygen † were among the first of those researches, and it was found that in nitrogen and hydrogen the velocities depended only on the ratio of the electric force Z to the gas-pressure p, but with oxygen the values obtained for the velocities U and W diminished as the force Z and the pressure p were increased in the same proportion. This was attributed to the formation of ions, as the ratio of the number of ions to electrons in the stream would increase with the pressure. The measurements made with the smaller gas-pressures were therefore taken as being approximately the velocities in oxygen, but the exact values of the velocities and the cause which led to the formation of the ions were not determined. It was therefore considered desirable to make further experiments with this gas, in order to find the velocities more accurately and to ascertain whether the formation of ions was due to an impurity in the gas, or is an effect which may occur in a very small proportion of collisions of electrons with molecules of oxygen.

* Communicated by Prof. J. S. Townsend, F.R.S.

† J. S. Townsend and V. A. Bailey, Phil. Mag. xlii. p. 875, Dec. 1921.

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In the above experiments the electrons were obtained by the action of ultra-violet light on a metal plate, and ebonite insulation was used in the construction of the apparatus. It therefore remained to make experiments where a hot filament is used to supply the electrons, in order to eliminate any effect which the ultra-violet light may have had on the gas, and to find whether the oxygen became impure owing to some action of the gas either on the ebonite insulation or on the elastic glue which was used to make air-tight joints in the outer case of the instrument.

2. No diminution was observed in the number of ions in a stream of electrons obtained from a hot filament; and after this had been established, the effect of impurities was investigated. For this purpose two improved forms of apparatus were used where the insulation was entirely of glass, and the joints of the outer case were carefully ground to fit, so that the gas should be exposed to as little of the elastic glue as possible. These instruments had been made for the experiments on monatomic gases, and they have been fully described in the account of the experiments made on the motion of electrons in argon and hydrogen by Professor Townsend and Mr. Bailey *. The results obtained with these two instruments were in good agreement, and it was found that with carefully prepared oxygen the number of ions in the stream of electrons obtained with ultra-violet light was quite inappreciable, even when comparatively large pressures of the gas were used.

3. As examples of the measurements, the results obtained with the instrument where the stream of electrons passed through a slit at two centimetres from the receiving electrodes may be considered. Examples of the values of W and k which were obtained are given in Table I., where the determinations are arranged in groups, corresponding to the cases where the ratios of Z/p were approximately the same. The quantity k is the ratio of the energy of agitation of the electrons to the energy of agitation of a molecule of a gas at 150° C., and the velocity of agitation U is obtained by the formula:

$$U = 1{\cdot}15 \,.\, 10^7 \sqrt{k}. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

It will be noticed that k and W are independent of Z and p, provided that the ratio Z/p is constant.

* J. S. Townsend and V. A. Bailey, Phil. Mag. xliv. p. 1033, Nov. 1922.

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TABLE I.—Oxygen.

Z/p.	Z.	p.	k.	W.10^{-5}.
·85	4·2	4·94	11·2	20·3
1·29	6·4	4·94	15·2	24·2
1·32	4·2	2·42	17·3	25·0
2·10	6·4	3·04	24·0	31·1
2·16	10·7	4·94	24·6	31·2
3·02	14·9	4·94	34·3	35·9
3·17	6·4	2·02	35·2	36·5
3·86	19·1	4·94	40·0	39·2
3·98	6·4	1·61	40·5	40·4
3·98	14·7	3·70	40·5	40·2
4·21	12·8	3·04	41·0	40·8
4·26	8·6	2·02	41·8	41·1
4·29	21·2	4·94	41·9	40·9
4·96	6·4	1·29	45·5	42·8
5·08	18·8	3·70	47·5	43·1
5·16	25·5	4·94	49·0	43·2
5·21	12·6	2·42	48·6	43·3
6·27	23·2	3·70	53·2	46·4
6·32	19·2	3·04	53·6	46·8
6·82	33·7	4·94	53·7	47·9
7·95	12·8	1·61	59·5	53·1
8·42	25·6	3·04	58·9	54·4
13·7	12·9	·94	70·9	73·1
14·1	42·7	3·04	73·4	74·9
17·1	16·7	·98	84·3	86·7
17·6	42·5	2·42	84·2	85·7
23·5	23·2	·98	102·5	112
23·8	38·2	1·61	100	114
33·3	42·9	1·29	118	148
33·5	23·3	·695	123	148
39·9	27·7	·695	131	172
40·1	38·5	·94	133	176
46·2	32·1	695	143	192
52·5	36·5	·695	155	215
58·6	40·7	·695	162	235

4. Another set of experiments was made with the apparatus where the electrons passed through a slit 4 cm. from the receiving electrodes, and a selection from the results obtained with this instrument is given in Table II.

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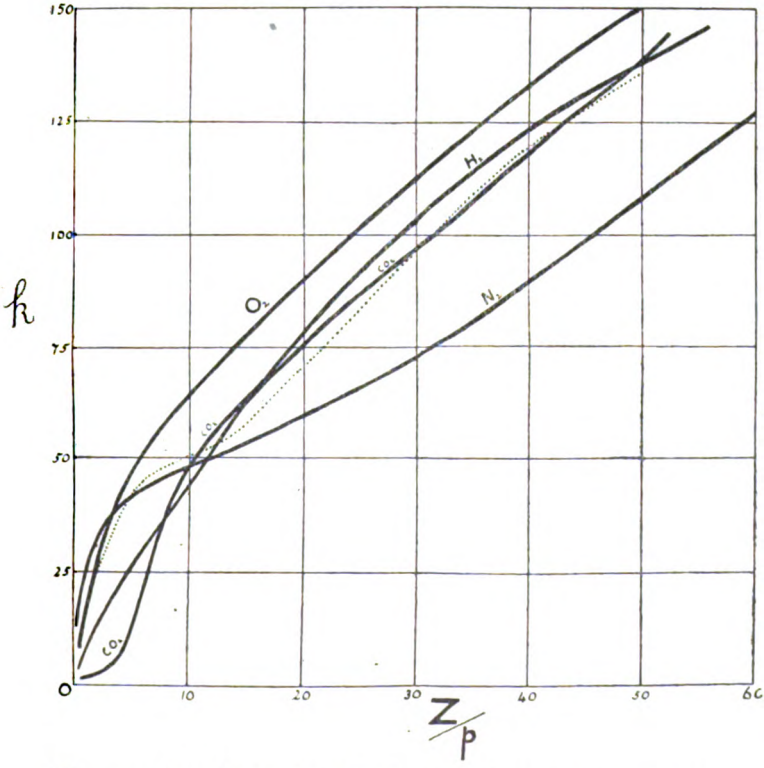
TABLE II.—Oxygen.

Z/p.	Z.	p.	k.	W . 10^{-5}.
·358	2·10	6·42	5·52	6·20
·430	2·10	4·82	6·47	10·6
·504	2·10	4·17	7·00	13·4
2·46	8·25	3·36	24·5	33·1
3·83	12·85	3·36	39·1	39·0
4·82	15·00	3·11	55·3	41·6
6·05	18·80	3·11	53·4	44·3
7·92	21·3	2·69	58·2	51·1
9·64	21·3	2·21	62·3	56·1
14·3	31·6	2·21	74·5	74·7
18·0	39·7	2·21	86·1	84·7

Fig. 1.



The results obtained with the two instruments are thus seen to be in good agreement, and may be represented by the curves given in figs. 1 and 2, in which the larger values of k and W are the ordinates and the ratio Z/p the abscissæ.

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Fig. 2.

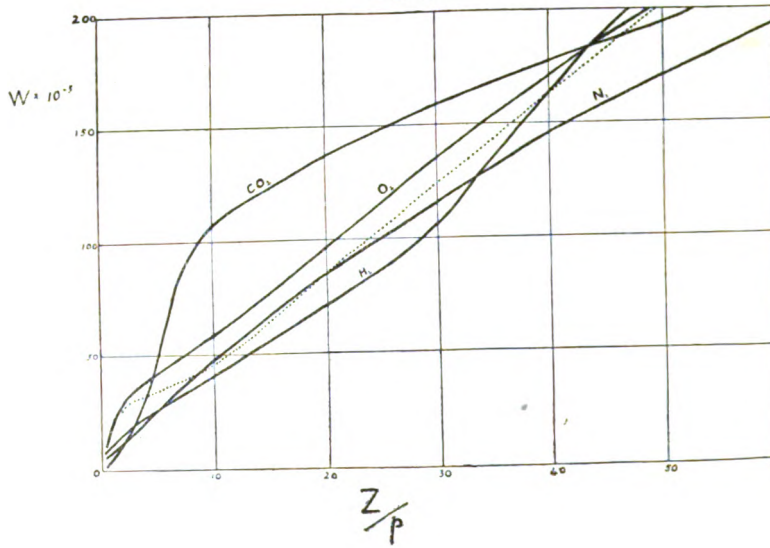
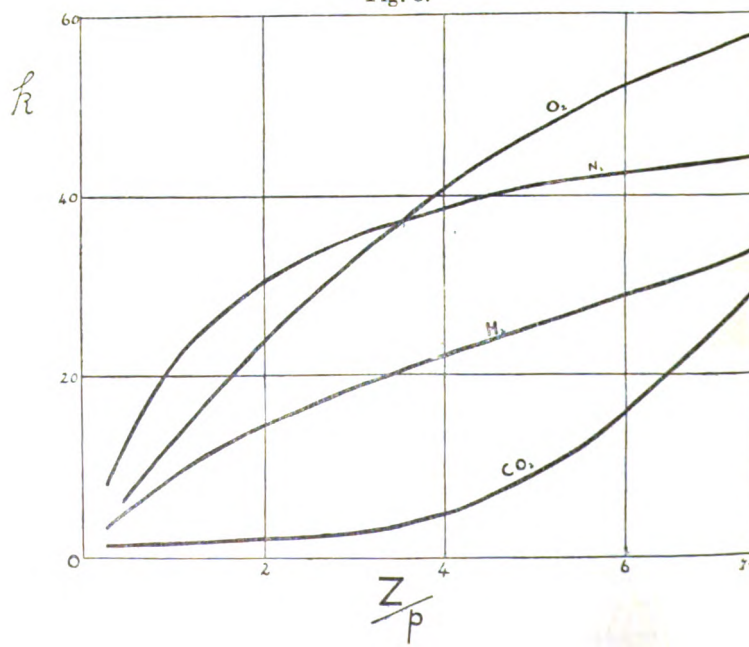


Fig. 3.



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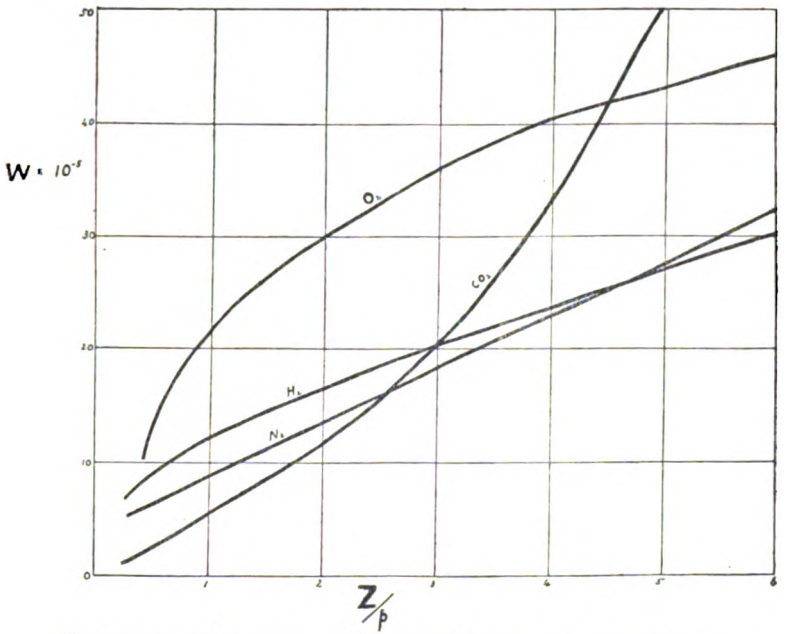
The electric force Z is expressed in volts per centimetre, the pressure p in millimetres of mercury, and the velocities W and U in centimetres per second. The smaller values of k and W are similarly represented by the curves in figs. 3 and 4.

Fig. 4.



For comparison, the corresponding curves for nitrogen, hydrogen, and carbon dioxide are also given, and the dotted curves represent the results obtained in the first experiments with the apparatus where the insulation was of ebonite. As indicated in the curves for oxygen the proportion of ions in the stream of electrons becomes smaller as the pressure decreases, for the difference between points on the dotted and continuous curves for the small value of Z/p becomes relatively less when Z is constant and p reduced.

An apparatus was also used in which the electrons were produced by a hot filament. It was first tested by making measurements with hydrogen. The results obtained with the filament are given in Table III. as k_1 and W_1. The neighbouring columns contain the values k_2 and W_2 which had been obtained earlier by Townsend and Bailey (*loc. cit.*) with an instrument where the electrons had been produced by the action of ultra-violet light.

These results agree within the error of experiment, which is less than 5 per cent.

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TABLE III.—Hydrogen.

p.	Z.	Z/p.	k_1.	k_2.	$W_1 . 10^{-5}$.	$W_2 . 10^{-5}$.
2·28	6·4	2·8	18·6	18·6	18·2	18·9
2·28	12·8	5·58	27·3	28·1	25·3	26·2
2·28	19·2	8·42	37·3	38·5	32·7	34·2
2·28	25·6	11·2	47·4	48·4	37·9	40·2
·26	12·8	49·2	142	147		
·26	19·2	73·8	192	193		

This proved that there could have been no action of the ultra-violet light which affected the measurements of U and W in hydrogen. It was found that a sufficient stream of electrons for making measurements in hydrogen with this instrument was produced when the filament was kept at a dull red glow.

When the instrument had been exhausted and washed out several times with pure oxygen, it was found that a sufficient stream of electrons was emitted in oxygen only when the filament was made to glow very brightly at a much higher temperature than in the case of hydrogen.

The velocities obtained in oxygen by using the filament as a source of electrons were generally smaller than those obtained in the earlier experiments with ultra-violet light, and were rather irregular. The results indicated that there was a number of ions in the stream which increased with the pressure. These effects were probably due to an impurity in the gas introduced by the action of the hot oxygen on wax used to make an air-tight joint near the filament.

5. The results of the experiments in which ultra-violet light was used are represented by curves (figs. 1 to 4) which exhibit the quantities k and W in terms of the ratio Z/p. The values of k and W corresponding to a series of values of the ratio Z/p are given in Table IV. The third column of the table gives the values of the velocities of agitation U of the electrons which have been calculated by means of the formula (1). The fourth column contains the corresponding values of the mean free path L obtained by the formula

$$W = \frac{ZeL}{pmU} \times \cdot 815,$$

where L is the mean free path of electrons moving with the velocity of agitation U in the gas at 1 millimetre pressure. The velocities W and U are in centimetres per second, L in centimetres, Z in volts per centimetre, and p in millimetres of mercury.

The manner in which L depends on U is shown graphically in fig. 5. The curves showing the relation between these

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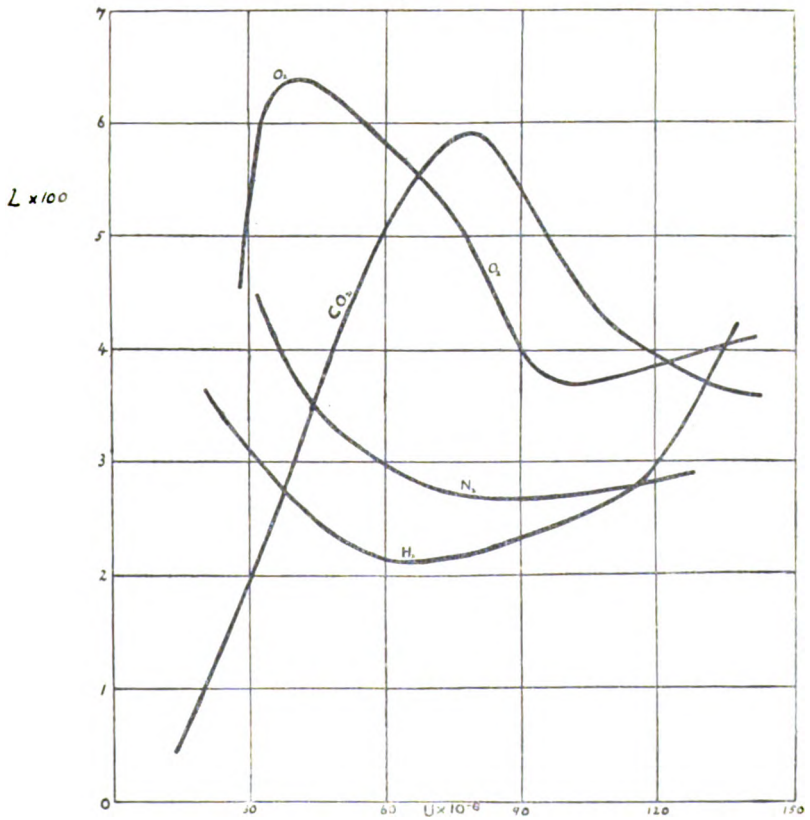
TABLE IV.—Oxygen.

Z/p.	k.	W . 10^{-5}.	U . 10^{-6}.	L×100.	λ×10^4.
50	150	205	141	4·05	521
40	133	172	133	3·99	414
30	113	136	123	3·87	303
20	90	98	109	3·74	199
15	77	78	101	3·67	147
14	74	74	99	*3·66*	138
13	72	71	97·6	3·73	130
12	69	67	95·6	3·74	121
10	64	60	92·0	3·86	105
7	56	50	86·1	4·31	83·0
5	47	43	78·8	4·89	73·0
2	24	30	56·3	5·91	69·8
1	13	22	41·3	*6·39*	69·1
·8	10·8	19	37·8	6·29	62·6
·6	8·4	16	33·4	6·22	56·6
·4	6	10	28 2	4·93	27·5

Fig. 5.



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quantities in the case of nitrogen, oxygen, and carbon dioxide are also given, as they have not previously been exhibited in this way.

The results for oxygen disclose the fact that, as the velocity of agitation of the electrons decreases from 14×10^7 to 10×10^7 cm. per sec., the mean free path becomes smaller and then gradually increases to nearly twice the value of its previous minimum, just as has been shown to be the case with the inert gases, in which the phenomenon is much more marked, and certain other gases to a less degree. In oxygen, however, a stage is reached when, as the velocity of agitation of the electrons decreases still further, the mean free path attains a maximum, after which it rapidly becomes smaller. A similar result was obtained by Skinker * in carbon dioxide.

Thus within a comparatively short range of velocities a maximum and a minimum value of the mean free path of electrons are obtained in oxygen. After this effect had been observed in oxygen, Skinker's experiments on carbon dioxide were repeated and his results were corroborated.

The minimum mean free path ·0366 cm. is obtained with the velocity 10^8 cm. per sec., which is the velocity acquired by the electron in moving in a field of 2·7 volts, and the maximum mean free path ·064 cm. is obtained with the velocity $4{\cdot}1 \,.\, 10^7$ cm. per sec. corresponding to ·48 volt.

6. The sixth column of Table IV. contains the values of the fraction λ of the mean energy of agitation $\frac{mU^2}{2}$, which is lost by an electron in a collision with a molecule of oxygen. These values were obtained from the formula :

$$\lambda = 2{\cdot}46 \,.\, \frac{W^2}{U^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

It is seen that λ increases with U. Some of the loss of energy in the collisions with the smaller velocities is probably due to dissociation of the molecules. This effect would occur before ionization by collision, as is seen from Kirkby's † experiments, which show that with small values of the ratio Z/p the number of molecules of oxygen which are dissociated exceeds the number ionized by collision.

7. The oxygen used in the above experiments was prepared by the electrolysis of a saturated solution of pure

* M. F. Skinker, Phil. Mag. xliv. p. 924 (1922).
† P. J. Kirkby, Phil. Mag. p. 559 (1908).

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barium hydrate. The limbs of the electrolysis tube were so constructed that the backward diffusion of hydrogen was rendered impossible. The oxygen was dried in several stages. It was first left for a day or more in contact with pure caustic potash. It was then dried three times in succession for shorter periods in phosphorus pentoxide, and was admitted into the main apparatus through a glass tube which was internally silvered, so that when communication with the mercury pumps and the McLeod gauge was cut off by a tap, the mercury vapour was gradually absorbed by the silver. Each apparatus was exhausted to a pressure less than $\frac{1}{500}$ mm., and was tested for air tightness over several weeks during vacation. No sign of a leak was registered on the McLeod gauge. Traces of impurity were removed by admitting oxygen to a pressure of at least 5 mm., which was pumped out to below $\frac{1}{500}$ mm. by means of a Gaede diffusion pump. This process was repeated several times until the percentage of impurity in the apparatus could be regarded as negligible.

The hydrogen used was admitted through a palladium tube after the apparatus had been exhausted. The carbon dioxide was prepared by heating some sodium bicarbonate. The order of the currents used in these gases was 10^{-12} ampere.

8. It may be of interest to draw attention to some attempts that have been made to account for the increase of the mean free paths of electrons as the velocity diminishes. F. Hund* has worked out an electrostatic field of force surrounding an atom which is such that almost all electrons of a certain small velocity are deflected by an amount 2π, and which leads to the existence of a maximum for L. He finds, however, that the power law of attraction near the nucleus of the atom disagrees with that roughly estimated from other data, and that argon should be the only gas which exhibits so pronounced an increase of L with U. He therefore assumes that, if the electron is moving so slowly that its deflexion, as calculated on the basis of classical electrodynamics, would entail a loss of energy greater than that actually possessed by the electron in the form of kinetic energy, it simply passes through the atom, which may thus be regarded as ring-shaped, the size of the inner circle of the ring increasing as the velocity U of the electron diminishes. By applying the ideas which H. A. Kramers †

* F. Hund, *Zeits. für Phys.* xiii. p. 241 (1923).
† H. A. Kramers, Phil. Mag. xlvi. p. 836 (1923).

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used in dealing with the emission of the continuous X-ray spectrum, he infers that, when an electron travelling along a rectilinear path collides with an atom, there is a certain probability of transition to a path of less energy which is also rectilinear, but that for decreasing values of U this probability rapidly becomes very small compared with L, so that a great number of electrons do not radiate during the collision; but remain in their stationary orbits and behave as if the atoms were not present. The reasoning does not appear to lead to a satisfactory quantitative result.

A second attempt to sketch a theory for the increase of L has been undertaken by Zwicky *.

He shows that the resources of the classical theory have not been exhausted by Hund, and that it is not necessary to have recourse to quantum methods to adduce an explanation which starts from comparatively simple assumptions. Like Hund, he restricts himself to considering inert gases which have no electron affinity. He calculates the deflexion experienced by an atom in colliding with four types of an atom, which are successively closer approximations to the true atom. Even when the atoms are regarded as being polarized by the electric field and having, in addition, a quadrupole moment, no increase of L occurs. He therefore adopts as his final approximation to the true atom a rotating dipole which excites an alternating field. On account of the phase relations that arise between the velocity of the electron and the period of the vibrations in the field, an increase of L with a decrease of U (in the terminology of this paper) becomes possible. By elementary considerations Zwicky shows that an electron which approaches a highly symmetrical atom pursues an ever-widening spiral path whose diameter is of the order of that of the atom when in close proximity to it, so that the electron may pass around and beyond it and need not go through it. A more complete knowledge of L at still lower electron velocities for a number of gases will be necessary before the nature of the collisions which occur will be sufficiently clear to enable an adequate theory to be set up.

The above researches were carried out in the Electrical Laboratory, Oxford. I wish to take this opportunity of thanking Professor Townsend for his valuable advice during the course of the work.

* F. Zwicky, *Phys. Zeitschr.* xxiv. p. 171 (1923).

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LVI. *Note on Saha's Ionization Formula, and on the Theoretical Value of the Photo-electric Absorption Coefficient.* By Prof. E. A. MILNE *.

CONSIDER an assembly of atoms in thermodynamic equilibrium at temperature T, whose ionization potential is χ_1. Let x be the degree of ionization, P_e the partial pressure of free electrons. Saha's formula † for the degree of ionization, as modified by R. H. Fowler ‡, is as follows:—

$$\frac{x}{1-x} P_e = \frac{(kT)^{5/2} e^{-\chi_1/kT} (2\pi m)^{3/2} \sigma}{h^3 b(T)} \quad . \quad . \quad . \quad . \quad (1)$$

Here h is Planck's constant, k Boltzmann's constant, σ is the "symmetry number" of the atom, and $b(T)$ is the partition function of the neutral atom given by

$$b(T) = q_1 + q_2 e^{-(\chi_1-\chi_2)/kT} + q_3 e^{-(\chi_1-\chi_3)/kT} + \ldots, \quad . \quad (2)$$

where $\chi_2, \chi_3, \ldots$ denote the energy-levels of the possible excited states of the neutral atom, and $q_1, q_2, q_3 \ldots$ are the *à priori* weights of the normal and the several excited states. It is assumed that no atoms are present in a higher degree of ionization. In this form the formula was cited by Fowler and Milne §, and it has been frequently re-quoted from the latter paper.

Unfortunately, as it stands (1) is not in general correct. It becomes correct on inserting a factor $b'(T)$ in the numerator on the right-hand side, where $b'(T)$ is the partition function for the ionized atom, and is given by a formula analogous to (2).

Formula (1) is correct in the case when $b'(T)=1$. Herein is the origin of the error. The corrected version is given in general terms in equation (9.94) of Fowler's original paper, but his investigation is usually explicitly confined to the case in which the ionized atom possesses no energy other than translational, *i. e.* to the case $b'(T)=1$. This is in fact true for ionized hydrogen, which Fowler considered in detail ||.

It is now easily seen that the appearance of the factors

* Communicated by the Author.
† Phil. Mag. xl. p. 479 (1920). ‡ Phil. Mag. xlv. p. 21 (1923).
§ Monthly Notices, R. A. S. lxxxiii. p. 407 (1923).
|| *Loc. cit.* section 7.

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$b(\mathrm{T})$ and $b'(\mathrm{T})$ is really an unnecessary complication; they disappear if we compare the numbers of ionized and neutral atoms in their normal states, instead of the whole numbers of ionized and neutral atoms. If n', n are the former numbers, q', q the weights of the normal states of the ionized and neutral atom, we have simply

$$\frac{n'}{n}\mathrm{P}_e = \frac{q'}{q}(k\mathrm{T})^{5/2}e^{-\chi_1/k\mathrm{T}}\frac{(2\pi m)^{3/2}\sigma}{h^3}. \quad . \quad . \quad . \quad (3)$$

If N′, N are the total numbers of ionized and neutral atoms,

$$\mathrm{N}' = \frac{n'b'(\mathrm{T})}{q'}, \quad \mathrm{N} = \frac{nb(\mathrm{T})}{q},$$

and the degree of ionization is given by

$$x = \frac{\mathrm{N}'}{\mathrm{N}+\mathrm{N}'}, \quad 1-x = \frac{\mathrm{N}}{\mathrm{N}+\mathrm{N}'},$$

and thus

$$\frac{x}{1-x}\mathrm{P}_e = \frac{b'(\mathrm{T})}{b(\mathrm{T})}(k\mathrm{T})^{5/2}e^{-\chi_1/k\mathrm{T}}\frac{(2\pi m)^{3/2}\sigma}{h^3}. \quad . \quad . \quad (4)$$

When the weights of the lowest state of the ionized and neutral atom are unequal, the correction will make an appreciable difference to the calculated degree of ionization. But I wish here principally to point out an important consequence of the correction, namely that it implies a correction to the formula for the coefficient of absorption of an atom beyond a series limit*, as given independently by Kramers † and the writer ‡.

The formula in question was deduced by the writer by equating the number of photo-electric ejections of electrons to the number of captures of electrons by ionized atoms. Let $\psi_r(\nu)\mathrm{I}_\nu d\nu dt$ be the probability that a neutral atom in a state r of weight q_r will in time dt, under the influence of isotropic ν-radiation of intensity $\mathrm{I}_\nu d\nu$, become ionized by

* The correction is of importance in the calculation of the general coefficients of absorption of an ionized gas: the writer has made this calculation, with the corrected formula, in Monthly Notices, R. A. S. lxxxv. June 1925.

† Phil. Mag. xlvi. p. 843 (1923).

‡ Phil. Mag. xlvii. p. 224 (1924). The same formula was also arrived at independently by Becker, but explicitly confined to the case of hydrogen, where the correction makes no difference (*Zeits. für Phys.* xviii. p. 333, 1923).

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absorption of a quantum of energy $h\nu$, with the emission of an electron of speed v given by

$$h\nu = \tfrac{1}{2}mv^2 + \chi_r, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where χ_r is the ionization potential in the r-state. The coefficient $\psi_r(\nu)$ is an Einstein probability coefficient, and is connected with the atomic absorption coefficient $\alpha_r(\nu)$ by the relation

$$\alpha_r(\nu) = \frac{h\nu\psi_r(\nu)}{4\pi}.$$

Further, let n_r be the number of atoms per unit volume in the r-state, n the number of ionized atoms in their lowest state, n_e the number of free electrons.

An application of the principle of detailed balancing of elementary processes (in this case, ejections and captures) then shows that

$$n_r\psi_r(\nu)\mathrm{I}_\nu\, d\nu\, dt$$
$$= 8\pi^2 n' n_e \left(\frac{m}{2\pi k\mathrm{T}}\right)^{3/2} e^{-\frac{1}{2}mv/k\mathrm{T}}\left[\mathrm{F}_r(v) + \mathrm{I}_\nu \mathrm{G}_r(v)\right] v^3\, dv\, dt, \quad . \quad . \quad . \quad (6)$$

where $2\pi\mathrm{F}_r(v)$ is the probability* of the unstimulated capture of a v-electron in the r-orbit by the ionized atom in its neutral state, and $2\pi\mathrm{I}_\nu\mathrm{G}_r(v)$ is the similar probability of a stimulated capture.

We now eliminate n'/n_r by the ionization equation

$$\frac{n'}{n_r}\mathrm{P}_e = \frac{q'}{q_r}(k\mathrm{T})^{5/2} e^{-\chi_r/k\mathrm{T}} \frac{(2\pi m)^{3/2}\sigma}{h^3}, \quad . \quad . \quad . \quad (7)$$

and substitute Planck's formula for I_ν. On applying (5), and imposing the condition that $\psi_r(\nu)$, $\mathrm{F}_r(\nu)$, $\mathrm{G}_r(\nu)$ must be independent of the temperature, we arrive at the formula

$$\alpha_r(\nu) = \frac{h\nu\psi_r(\nu)}{4\pi} = \frac{q' m^2\sigma}{2q_r} \cdot \left(\frac{c}{h\nu}\right)^2 2\pi\mathrm{F}_r(v). \quad . \quad . \quad (8)$$

This differs from the formula previously given by the writer and from the formula derived by a somewhat different method by Kramers, by the factor q' in the numerator for the weight of the normal state of the ionized atom †. It should be mentioned that the less rigorous method used by Kramers lends itself only with difficulty to the making

* More strictly, the effective cross-section of the atom for captures of the kind in question.

† The form of (8), taking account of relativity mechanics, is in effect given by Dirac, Proc. Roy. Soc. cvi. A. p. 581 (1924).

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of the correction; but Kramers's own application of the formula is unaffected, as he used it for the case in which the system after ionization is a bare nucleus, for which $q'=1$.

If it is possible for the collision of an electron with an *excited* ionized atom to result in capture in the r-orbit, then conversely it must be possible for an atom in the r-state to become ionized by the absorption of a quantum of radiation sufficiently large to leave the atom excited. The corresponding contribution to the atomic absorption coefficient would be given by (8) on introducing an appropriate value for q', namely the weight of the excited state of the ionized atom. But the capture-probability factor $F(v)$ would probably be very small.

Summary.

Saha's formula for high-temperature ionization requires a factor (partition function) relating to the *à priori* weights of the stationary states of the ionized atom, as well as the factor relating to those of the neutral atom introduced by Fowler. The formula for the photo-electric absorption coefficient requires similarly a factor for the weight of the lowest state of the ionized atom, as well as the factor for the weight of the neutral atom given by Kramers, Becker, and the writer. In all cases a ratio of weights is necessarily involved.

[ADDENDUM.—Kramers's deduction of formula (8) depends on considering an enclosure containing a single neutral atom and calculating the ratio of the probability that the atom is in its normal state to the probability that a given electron is missing and moving free with a given velocity. Apart from the difficulty of justifying the applicability of probability considerations to a single atom in this way, it is clear that the weight of the appropriate state of the ionized atom would make an appearance in the final formula, provided we compared the probability that the atom is neutral and in a given state with the probability that the same atom is ionized and in a given state; the ratio of the weights would then necessarily occur. In the more rigorous statistical discussion, the partial pressure of the free electrons has been shown in fact to be irrelevant*, and this suggests that Kramers's method of considering the free electron is not justifiable.

Trinity College, Cambridge,
May 1925.

* Phil. Mag. xlvii. p. 225 (1924).

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LVII. *Reply to Mr. U. Doi's "New Discussion of Bucherer's Experiment."* By A. H. Bucherer, *Doctor of Science, Professor of Theoretical Physics* *.

In this Magazine Mr. U. Doi has published a new discussion of the experiments carried out by me for the purpose of ascertaining the law of mass variability. The aim of Mr. Doi has been to establish an agreement between my experimental results and a formula of his own, which he derives from his anti-Einsteinian theory of relativity. He finds for the specific charge of the electron :

$$\frac{e}{m} = \frac{e(1-\beta^2)}{m_0}, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

while my experiments prove the Lorentz formula :

$$\frac{e}{m} = e\frac{\sqrt{1-\beta^2}}{m_0}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where, as usual, β signifies the ratio of the velocity of the electron to that of light.

The latter formula has subsequently been confirmed by other investigators. I refer to the work of my assistant, Mr. K. Wolz, to that of Neumann and of Cl. Schaefer, of E. Hupka and of Ch. Guye. It seems to me there cannot be a reasonable doubt as to its correctness. According to my original plan, one single radiographic curve should have sufficed to establish the law of mass variability. But it turned out that the trace of the curve at points of small deflexions resulted from two superimposed effects, the one being the radiographic action of the β-rays on which the forces acting between the condenser plates were balanced, and the other where they were not balanced.

Now the original theory of the experiment referred to the compensated rays corresponding to large deflexions; and as the theory of the non-compensated rays appeared at that time intricate and difficult, I decided to produce a number of radiographic curves whose maxima were so calculated as to represent varying velocities of the electrons. Only these maxima were measured, and from them the mass variability was deduced with the assistance of the constants of the apparatus and of the electromagnetic data.

* Phil. Mag. xlix. p. 434 (1925).

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Recently Mr. T. Lewis * has developed the complete theory of the curve, taking in account all factors that condition the trace. In future, then, it will be possible to demonstrate the validity of the Lorentz mass formula from a single radiogram. Unfortunately, the experimental films I could place at Mr. T. Lewis's disposal were too scanty, and in consequence the Lorentz formula could only be established up to velocities of $\beta = 0{\cdot}8$.

Comparing Mr. Doi's interpretation of the curve with that of Mr. Lewis, it becomes evident at once that the former by neglecting the most important factors at work in producing the trace cannot be accepted as proving any mass formula. I refer the reader to Mr. Lewis's exceedingly interesting paper.

It may not be superfluous to state that today the confirmation of the Lorentz formula can no longer be adduced as proving the Einsteinian theory of relativity. As Mr. P. Lenard has shown, this mass formula results from a very simple application of mechanics. For, putting for the total energy E of a mass m the expression which Hasenöhrl derived from the Maxwellian theory,

$$E = mc^2,$$

where c signifies the velocity of light; and equating this change of energy in unit time to the change of kinetic energy of the mass moving with velocity v, we obtain at once

$$\frac{dE}{dt} = \frac{vd(mv)}{dt}.$$

$$\therefore \quad m = \frac{m_0}{\sqrt{1-\beta^2}}.$$

Mr. Doi in concluding his paper proposes a value for the specific charge of the electron $\frac{e}{m_0}$ obtained by Prof. A. Sommerfeld by applying the special theory of relativity to the spectroscopy of hydrogen and helium. However, this application to the motion of the electrons within the atom is certainly not permissible, and the agreement between his theory and the spectroscopic data is only apparent.

Bonn, June 6th, 1925.

* Thos. Lewis, B.Sc., Proc. Roy. Soc. A. vol. cvii. pp. 544–560.

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LVIII. *On the Transmission of Air-Waves through Pipes.* *By* L. F. G. SIMMONS, *B.A., A.R.C.Sc., and* F. C. JOHANSEN, *B.Sc., of the Aerodynamics Department, National Physical Laboratory* *.

INTRODUCTION.

THE technique of air-speed measurement by means of pressure tubes has received considerable attention in recent years, and with the sensitive pressure gauges now available no difficulty is experienced in determining, to a high degree of accuracy, the speed of steady air-currents. In studying unsteady currents, such as natural winds, continuous records may be obtained by connecting the open ends of the pressure tubes to opposite sides of a specially constructed diaphragm gauge made with light moving parts and possessing a high natural frequency. But these records may fail to indicate the actual pressure changes which occur at the open ends on account of the wave-motions induced in the tubes being influenced by the viscosity of the air and by the volume of air enclosed in the gauge. Both factors exert a sensible influence on the results, and where long pipes of small diameters are employed they may lead to serious errors in the estimation of wind speed.

Some idea of the magnitude of the errors involved in certain simple cases representative of gusts and periodic flow is provided from experiments recently conducted at the National Physical Laboratory on the transmission of waves through rubber pipes. Grouped under two headings, the experiments deal (1) with the propagation of a single wave resulting from the sudden application of a known pressure at one end of the pipe, and (2) with waves generated by simple harmonic variations of pressure or displacement, applied at one end. The results pertaining to closed pipes indicate the relationship existing between the pressures at any instant at the two ends, and the extent to which these are affected by size and length of pipe, and by the type of gauge used; whilst measurements of the displacement made at the end of open pipes may be compared with calculations based on the theory given by Lord Rayleigh. This theory (which was propounded in relation to acoustic problems) is of course subject to the usual limitations: (1) that the maximum velocity must

* Communicated by Mr. R. V. Southwell, F.R.S.

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be small compared with the velocity of sound, (2) that $\frac{VD}{\nu}$ must not exceed a certain limit. Uniform motion across each section is presupposed, except within a thin boundary layer in the immediate neighbourhood of the wall, and this assumption imposes a further limitation upon the theory, restricting its application to pipes larger than a certain minimum diameter; for when the thickness of the boundary layer becomes comparable with the diameter the distribution across the section cannot remain uniform. There is reason to believe that the conditions assumed are realized in the experiments made with pipes of ·475 cm. and ·950 cm diameter; hence any comparison between experimental and theoretical results is valuable, not only in showing the deficiencies of the existing theory, but also as a basis of reference for checking future theories.

A rough survey of the results shows that (except where resonance occurs, as with pipes of ·95 cm. diameter) the transmitted pressure is less than that applied, and is subject to a lag in phase which delays the reception of the wave at the far end. As a general rule it may be taken that a reduction in the pressure amplitude, together with an increased phase lag, are produced by:

(i.) an increase in length of pipe,
(ii.) a decrease in diameter,
(iii.) an increase in frequency.

Where comparisons have been made, large discrepancies exist between the experimental and calculated values. In some cases the comparisons are perhaps hardly legitimate, since the end conditions required for a simple solution of the equations of motion were only approximately fulfilled by the apparatus employed; but in other cases, where no doubts of this nature exist, the evidence shows that the present experiments do not fall within the range of applicability of Rayleigh's theory. Lastly, the experiments demonstrate the unsuitability of the ordinary type of diaphragm gauge for recording, in detail, rapidly changing pressures such as occur during rapid manœuvres of aircraft, or in natural winds during gusty weather, and point to the need of a new form of gauge of small internal volume.

The present communication is divided for convenience into three parts. The first is devoted to a review of the Rayleigh theory of wave-motion through pipes; the second deals with experiments in which pressures were measured

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with a diaphragm gauge; and the third with later experiments in which more refined means of measuring pressure and displacement were introduced.

Part I.—Review of Theory.

Apart from the results of a few rough experiments, no data appear to be available relating to the effects of viscosity on the transmission of air-waves through pipes. On the theoretical side, the subject has received some attention from a number of physicists—notably Stokes, Kirchhoff, and Rayleigh,—but there is no experimental verification, as far as the writers are aware, of their calculations for the wave-motion produced by simple harmonic variation of the pressure or the displacement at one end of a pipe.

Rayleigh's elementary theory of wave propagation along a pipe is based on the assumption that the motion is wholly longitudinal and approximately uniform across any section, except near the wall where viscosity exercises a sensible influence. On the ground that the boundary layer so affected is small in comparison with the diameter of the pipe, he concludes that the viscosity forces may be calculated from Stokes's formula for the drag of an infinite plate when executing harmonic vibrations in a plane parallel to its own. The equation of motion for waves of frequency n, established in the usual manner from considerations of the forces acting on a small element of the fluid contained between two sections δx apart, is shown to be

$$\left(1+\frac{P}{S}\sqrt{\frac{\nu}{2n}}\right)\frac{\partial^2\xi}{\partial t^2}+\frac{P}{S}\sqrt{\frac{\nu n}{2}}\frac{\partial\xi}{\partial t}=a^2\frac{\partial^2\xi}{\partial x^2}\text{*}, \quad . \quad (1)$$

where ξ denotes the displacement of the fluid at section x,

ν is the coefficient of kinematic viscosity,

P = perimeter, and S = cross-sectional area of pipe.

$a=\sqrt{\frac{p_0\gamma}{\rho_0}}$ = velocity of sound in air,

γ = ratio of specific heats of air.

* Rayleigh's 'Sound,' vol. ii. 1896 edition, p. 318. The equation given by Rayleigh has been slightly modified by the substitution of ξ for $\frac{X}{S}$.

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A solution of (1) may be obtained in the form

$$\xi = \Sigma A e^{int \pm mx}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

provided that

$$a^2m^2 = -\left(1+\sqrt{\frac{\nu}{2n}}\cdot\frac{P}{S}\right)n^2 + i\sqrt{\frac{\nu n}{2}}\cdot\frac{P}{S}n, \quad . \quad . \quad (3)$$

where the two roots of m may be written $\pm(p+iq)$.

Making this substitution in (2), we have

$$\xi = \Sigma A e^{int \pm (p+iq)x}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

A particular form of this solution, applicable to the present problem (since it represents the combined effects of the incident and reflected waves) is

$$\xi = Ae^{-px}\sin(nt-qx) + Be^{-p(2l-x)}\sin\{nt-q(2l-x)\}$$
$$+ Ce^{-px}\cos(nt-qx) + De^{-p(2l-x)}\cos\{nt-q(2l-x)\}, \quad (5)$$

where A, B, C, and D are arbitrary constants to be determined from the specified terminal conditions, and l = total length of pipe. With the aid of the relation

$$p - p_0 = -p_0\gamma\frac{\partial\xi}{\partial x},$$

equation (5) can be used to calculate the pressure at any point in excess of the normal pressure p_0.

On the assumption that $\xi = \xi_0 \sin nt$ at $x=0$, two cases of immediate interest arise :—

Case 1. *Free End.*—The condition to be satisfied at $x=l$ is $\frac{\partial\xi}{\partial x}=0$. Hence we have

$$A = B, \quad \text{and} \quad C = D;$$

$$\therefore \quad \xi = Ae^{-px}\sin(nt-qx) + Ae^{-p(2l-x)}\sin\{nt-q(2l-x)\}$$
$$+ Ce^{-px}\cos(nt-qx) + Ce^{-p(2l-x)}\cos\{nt-q(2l-x)\}, \quad . \quad . \quad . \quad (6)$$

where A and C are determined by substituting $\xi = \xi_0 \sin nt$ for $x=0$ in (6), and afterwards equating coefficients of $\sin nt$ and $\cos nt$.

Case 2. *Fixed End.*—The condition for a fixed end is

$$\xi = 0 \text{ at } x = l.$$

We now have

$$A = -B, \quad \text{and} \quad C = -D;$$

$$\therefore \quad \xi = Ae^{-px}\sin(nt-qx) - Ae^{-p(2l-x)}\sin\{nt-q(2l-x)\}$$
$$+ Ce^{-px}\cos(nt-qx) - Ce^{-p(2l-x)}, \cos\{nt-q(2l-x)\}, \quad . \quad . \quad . \quad (7)$$

where, as before, A and C are determined from the condition

$$\xi = \xi_0 \sin nt \text{ at } x = 0.$$

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Again, substituting $\frac{\partial \xi}{\partial x}$ from (7) in the relation

$$p - p_0 = -p_0 \gamma \frac{\partial \xi}{\partial x},$$

we obtain the following expression for the excess pressure at the fixed end:

$$p - p_0 = 2\xi_0 e^{-pl} \gamma p_0 \sqrt{\frac{p^2 + q^2}{(1 - 2e^{-pl} \cos 2ql + e^{-4pl})}} \sin (nt - ql + \theta), \quad . \quad . \quad . \quad (8)$$

where

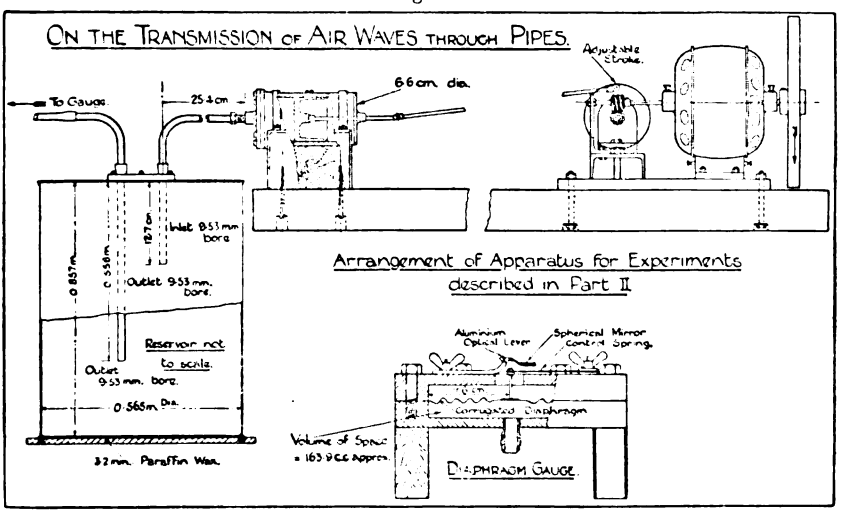
$$\tan \theta = \frac{e^{-2pl}(p \sin 2ql + q \cos 2ql) - q}{e^{-2pl}(p \cos 2ql - q \sin 2ql) - p}.$$

Part II.—Measurements of Pressure by means of a Diaphragm Gauge.

(a) *Experiments on the Propagation of Single Waves.*

A preliminary series of experiments was conducted with the object of determining the influence of viscosity on the

Fig. 1.



propagation of a wave along a pipe due to a pressure suddenly applied at one end. The essential features of the apparatus comprised an air-tight reservoir of about 50 litres capacity connected by rubber pipe to the diaphragm gauge illustrated in fig. 1. A second connexion to the reservoir,

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closed with a cock, enabled the pressure of the contained air to be raised to a pre-determined amount above atmospheric, usually not greater than 2 cm. of water. The gauge consisted of a chamber having a volume of about 160 c.c. closed by a corrugated metal diaphragm. A flat adjustable spring provided an additional control and enabled the sensitivity to be varied within certain limits. The motion of the diaphragm was indicated by an optical lever, made with light moving parts so as to reduce the inertia effects to a minimum, and designed to give an angular movement of the mirror proportional to the vertical displacement of the diaphragm over a range of $\pm 1{\cdot}3$ cm. of water. The natural frequency of the instrument was much higher than the frequencies common to the experiments, and the inertia effects, even in the extreme case of a sudden application of pressure to a short length of pipe, were shown to be negligible.

Observations of the deflexion of the gauge were made photographically by means of a roll-film camera operated by an electric motor, the time-scale being provided by the movement of a shutter, electrically actuated by a Weston relay, which interrupted a beam of light at uniform intervals during the unrolling of the film. In making an experiment the pressure in the reservoir was raised by admitting air at higher pressure through the by-pass into the reservoir, the gauge connexion being meanwhile stopped at the reservoir end. The film was then started, and the reservoir put into rapid communication with the gauge by means of a quick-release device.

The results of these preliminary experiments are presented in fig. 2 as curves of pressure on a time base, supplemented by Table I., which shows the time-intervals required by the pressure at the far end to reach 90 per cent. of its maximum value. They illustrate in a striking manner the influence of viscosity in delaying the growth of pressure at the far end. This final pressure is approached asymptotically, and the time-interval required depends upon the diameter and the length of the pipe; it is found to be independent of the magnitude of the pressure itself, as would be expected in the light of dimensional theory. Thus, referring to the accompanying Table I. (in which the times taken for the pressure to reach 90 per cent. of the maximum value are taken as a standard of comparison), we see that an increase in the diameter from 3·99 to 6·35 mm. reduces the time-interval from 7·8 to 1·05 secs.; a decrease in length from 30·79 to 15·24 m. is accompanied by a reduction in time from 8·2 to 6·1 secs.; but an alteration

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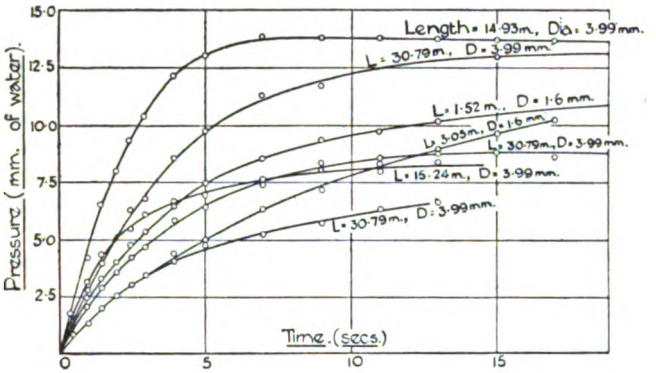
in the initial pressure from 8·76 to 12·95 mm. of water produces no appreciable change in the time. It should be stated that the figures refer to time measured from the instant of reception of the wave at the far end (that is to say, the instant at which the diaphragm starts to

Fig. 2.



Experimental Results illustrating the Growth of Pressure at the far end of a pipe due to the sudden application of pressure at the near end.

record); there is necessarily an interval between starting and receiving the wave, but this is small, since the measurements indicated that the velocity of propagation in the smallest pipe was probably not less than 91 m./sec.

TABLE I.

Length (metres).	Pipe Int. Diameter (mm.).	Applied Pressure (mm. of water).	Time (seconds).
30·79	3·99	11·77	7·8
31·70	6·35	11·77	1·05
30·79	3·99	8·76	8·2
30·79	3·99	12·95	8·4
15·24	3·99	8·25	6·1

(b) *Waves produced by a simple harmonic pressure variation.*

The apparatus employed for the second series of experiments is illustrated in fig. 1. It consisted of an airtight reservoir of about 215 litres capacity, connected

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by the rubber pipe under experiment to the diaphragm gauge. The oscillating movement of a piston in a cylinder connected to the reservoir alternately compressed and expanded the enclosed air. Both the amplitude and the frequency of the pressure changes could be readily varied, but in general the pressure variation was restricted to the range ± 1 cm. of water at frequencies below 2·5 per second, the mean pressure throughout remaining atmospheric.

Measurements of transmitted pressure were made by observing the motion of a beam of light, reflected from an optical lever on the gauge to a scale placed about 4·5 metres away. To obviate errors arising from irregular movements of the zero (due either to barometric or temperature changes) the complete traverse of the spot of light from side to side was noted, and the mean value of a large number of oscillations was accepted as representing the maximum range of pressure for the frequency under investigation. From observations of the position of the reflected beam at the instant when the piston reached one end of the stroke, rough estimates were made of the phase-displacement between the forcing motion and the pressure at the gauge; these measurements were greatly facilitated by the use of a second beam of light actuated by an electric contact fixed to the piston rod in such a position that the light became visible as a flash on the scale when the piston reached its extreme position.

This series of experiments provides measurements of the pressure at the far end of rubber pipes up to 122 metres in length produced by a harmonic variation of imposed pressure. Details of the amplitude and phase relationships existing between the transmitted and impressed values are afforded by the curves of figs. 3 and 4, which refer to pipes of 4·75 mm. and 9·53 mm. bore respectively. It should be mentioned that the figures indicating the length of pipe refer in all cases to the length, including that of a short reduction piece, beyond the outlet pipe from the reservoir.

An examination of these curves reveals several important features: in the first place it is seen that, for a given frequency, the amplitude of the transmitted pressure is in general smaller than that of the applied pressure; and, in the second, that the transmitted pressure is diminished by a reduction of pipe diameter, as is evident from a comparison of the curves of figs. 3 and 4. Further, fig. 4 clearly indicates the occurrence of resonance in pipes of 9·53 mm. diameter, and shows the influence of pipe-length

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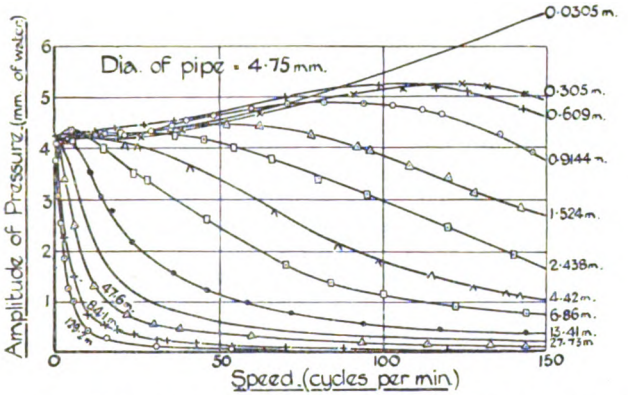
Fig. 3.



Variation of Transmitted Pressure with Frequency for pipes of various lengths due to a simple harmonic pressure applied at the near end.

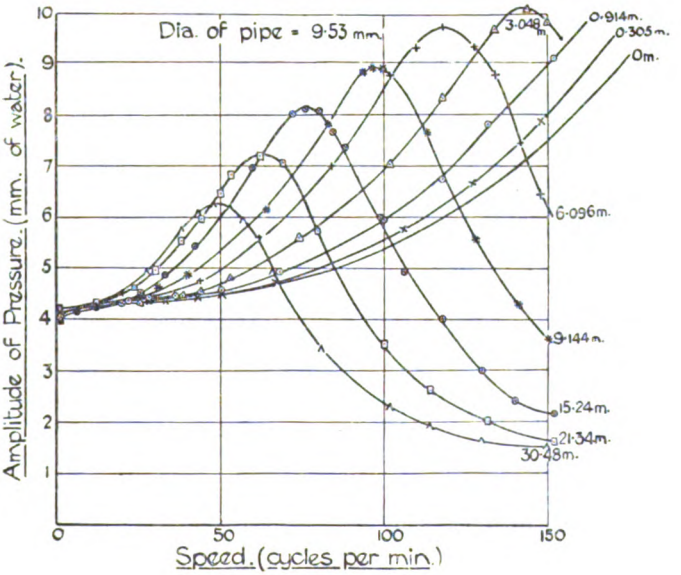


Fig. 4.

in modifying the maximum amplitude. From a consideration of fig. 4 it is apparent that even with the shortest pipe—viz., the outlet pipe from the reservoir (about 0·813 m. long and 9·53 mm. bore)—the rise of transmitted pressure

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with an increase in the speed of fluctuation indicates an approach to a condition of resonance: on this account an allowance must be made for the presence of the outlet pipe in any comparison undertaken between the different results. The curve designated 0 m. in fig. 4 has been taken (for purposes of calculation) to represent the standard pressure at the near end of the pipe for different frequencies. From a few experiments, the results of which are not here included, a lag in phase was observed between the impressed and transmitted pressures. This phase displacement was found to increase in magnitude with an increase in the length and a decrease in the diameter of the pipe.

Comparison with Theory.—In a number of cases, values for the pressures have been calculated by the use of Rayleigh's formula (see Part I.), and these, together with the corresponding observed values, are given in the following Table :—

TABLE II.

Frequency (cycles per minute).	Pipe.		Pressure (mm. of water).	
	Internal Diameter (mm.).	Length (metres).	Calculated.	Observed.
50	1·6	0·76	4·57	0·56
50	1·6	2·59	4·54	0·13
50	3·175	6·10	4·62	1·17
50	3·175	24·38	5·48	0·25
50	4·75	6·10	4·59	2·43
50	4·75	24·38	5·28	0·64
50	9·53	6·10	4·59	4·93
50	9·53	24·38	5·08	6·55

Note.—In all calculations a value of 0·144 in c.g.s. units has been taken for the kinematic viscosity of air.

The discrepancies existing between calculated and observed values are too large to admit of any useful comparison being made between the two sets, and suggest the desirability of investigating the terminal conditions existing in the pipe.

An estimate of the compression of the air in the gauge caused by a pressure of about the magnitude met with in the experiments shows that there is an appreciable movement of air at the far end of the pipe. The assumption, therefore,

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that the gauge constitutes a fixed end is useful only for purposes of rough comparison. An attempt was made to calculate the effect of the motion of the air into the gauge on the recorded pressure, but although the correction from this cause was found to be so large as to indicate the importance of making a similar allowance in all cases where fluctuating pressures are measured by means of a diaphragm gauge, it cannot account for the wide divergence between the calculated and observed results.

The same conclusion can be drawn with regard to a correction for the conditions obtaining at the near end of the pipe. Further, the difficulty of estimating with any certainty the complex behaviour of the air in the reservoir makes it advisable to conduct experiments with a modified form of apparatus rather than to introduce a further correction factor which will probably account for no more than a small proportion of the discrepancy. A consideration of these experiments furnishes the subject matter of Part III.

Part III.—Measurements of Pressure by means of Alcohol Manometers.

In order to obviate the difficulties inherent in the use of the reservoir and diaphragm gauge, modifications were made in the apparatus so as to secure conditions at the ends of the pipe under experiment capable of mathematical expression, to as close an approximation as possible. The reservoir at the near end of the pipe was dispensed with, the experimental pipe of 9·53 mm. diameter being directly connected to a cylinder of the same bore. By means of a piston and crank mechanism, a definite simple harmonic displacement of the air could be secured at the near end: the amplitude could be readily varied within fairly wide limits, but most of the measurements were obtained with a piston-stroke of 29 mm.

Of the several attempts to measure pressure whilst maintaining approximately zero displacement of the air at the far end of the pipe, the most successful involved the use of a liquid manometer consisting of a glass tube of small diameter (about 2 mm.) supported vertically with its lower end below the free surface of alcohol contained in a vessel of much greater diameter (about 25 mm.). Reliable results were obtained with this type of gauge at the lower speeds, but at higher speeds the readings were influenced by the inertia and viscosity of the alcohol.

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To calculate the corrections required, it is necessary to suppose that the column of liquid oscillates through a small range $\pm a$ about a mean position distant l from the end, under the action of an applied pressure $p \sin nt$. On the reasonable assumptions that the resulting force due to surface tension remains unchanged and that the mass of oscillating liquid is constant, the equation of motion is easily seen to be

$$\rho(l+a)\frac{d^2x}{dt^2}+k(l+a)\frac{dx}{dt}+g\rho x = p \sin nt,$$

where the first two terms represent the relatively small forces due to inertia and viscosity respectively: thus p can be determined from the known solution of the equation. Clearly, this method leads only to an approximate estimate of the corrections; hence the numerical results given for pressures at the higher speeds do not represent the same degree of accuracy as those at the lower speeds.

The coefficient of viscosity, k, appropriate to the motion was determined from oscillation experiments with a U-tube partly filled with alcohol: a value of 35 c.g.s. units found from these experiments has been taken for the purpose of the calculations.

Open-ended pipes.—The displacement of the air at the open end was made apparent by the motion of a soap-film introduced into a glass tube, about 20 cm. in length and about 12·7 mm. in diameter, connected to the end of the pipe. When at rest, the film formed a thin diaphragm across a section about half-way along the tube; during an experiment it oscillated about this position with an amplitude which in some cases approached 5 cm. To obtain satisfactory results it was found necessary to keep the wall of the tube wet with the soap solution: this reduced the resistance to motion and at the same time tended to preserve the existence of the film, which generally lasted for less than a minute. With precautions taken to secure the best conditions, the maximum resistance at the highest speeds was less than a pressure of 1·25 mm. of water: in other words, the far end did not accurately conform to the conditions of a free end owing to the existence of this extraneous pressure. Rough calculations show, however, that the maximum error from this cause is probably less than 6 per cent. of the observed value of the displacement. It should be added that the dis-

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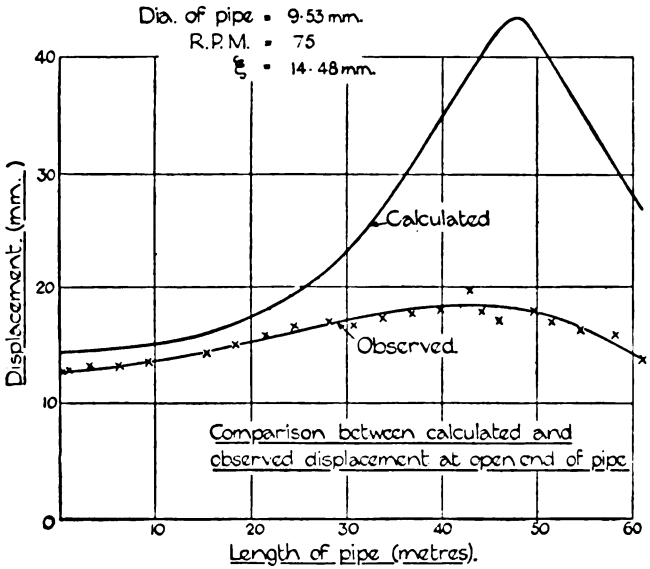
placements could be measured in the majority of cases to within 0·5 mm. (*i.e.* about 1 per cent.), and that the film results were subsequently checked by observing the motion of smoke injected into the tube.

Fig. 5 shows the variation of amplitude with length of pipe at a constant speed (R.P.M. = 75) resulting from a forced motion ($\xi = 14{\cdot}5 \sin 7{\cdot}85t$) imposed at the near end. Theory and experiments indicate a critical length of pipe (in the neighbourhood of 46 metres) at which the dis-

Fig. 5.



placement reaches a maximum; but whereas the observed value of this displacement is 19 mm., the figure calculated from equation 6 (p. 556) is 44·4 mm. This difference is not likely to be materially reduced if an allowance is made for the pressure required to overcome the resistance opposing the motion of the film, since in the particular case ($l = 0$) the difference from this cause is only about 10 per cent. of the observed value. Further evidence of the want of concordance between the two sets is seen in the accompanying Table of results pertaining to a pipe of length 30·5 metres and 9·53 mm. diameter.

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TABLE III.

R.P.M.	Amplitude of Displacement (mm.) at far end of 30·48 metres pipe. Calculated.	Observed.
25	15·24	14·47
75	21·2	19·55
115	33·78	26·42 (max.)
155	82·55 (max.)	15·49
180	38·61	——

These figures are of interest in showing that both the calculated and observed values for the displacement increase with frequency up to a certain point where a maximum

Fig. 6.

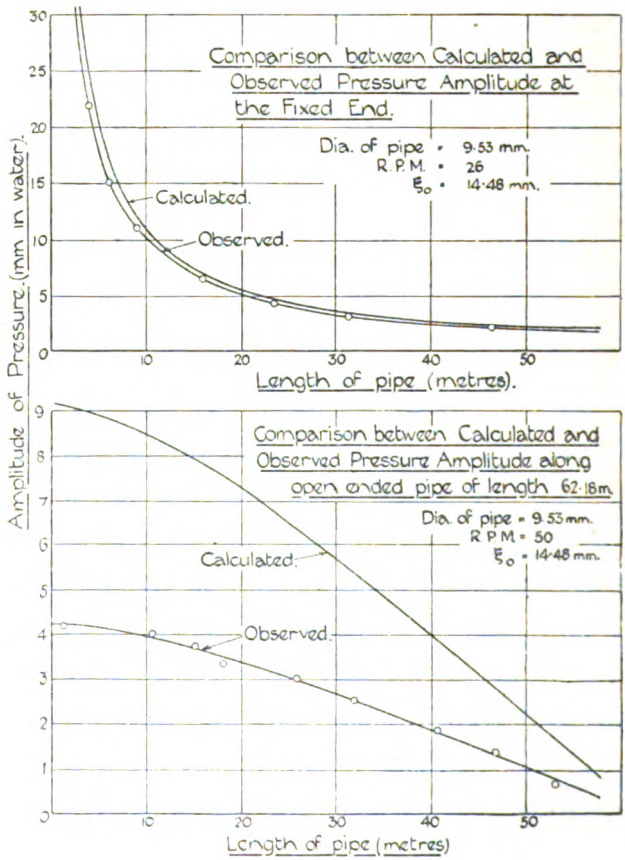

Fig. 7.

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value is reached. In contrast, however, with the curves of fig. 5, where the observed and calculated maxima are seen to occur at about the same lengths of pipe, the maxima here occur at widely different frequencies.

In figs. 6 and 7 amplitude of pressure is plotted against length of 9·53 mm. bore pipe for the two conditions of fixed and open end respectively. The pressure was measured at the end of the closed pipe, and at intermediate points along the open-ended pipe. In both cases the curves of calculated and observed pressures are of similar shape, the calculated values being, as before, larger than those observed. The close agreement noticeable in fig. 6 may reasonably be ascribed to the low frequency of oscillation (26 cycles per minute), and provides an interesting confirmation of the effects of frequency on viscosity and inertia losses, as mentioned in the preceding paragraph.

The curve of observed values plotted in fig. 7 is obtained from fig. 8 by cross-plotting, and provides a typical example of the variation of pressure along an open-ended pipe for frequencies not exceeding 60 per minute. In the example given, the pressure attains a maximum at or near the piston end; but it will be observed that at higher frequencies the maximum pressure occurs at other positions nearer the open end. There is a marked disparity between the calculated and observed values, which clearly demonstrates the need for a revised theory in closer agreement with observed facts.

Fig. 8 shows the relationship between frequency and pressure, measured at various distances from the near end, in an open pipe 62·18 m. in length and 9·53 mm. in diameter. For points within 18 metres of the near end the curves show the same characteristic feature of pressure amplitude increasing with rapidity of fluctuation up to a maximum value in the neighbourhood of 60 cycles per minute; from thence to about 120 cycles the pressure decreases slightly, but at higher speeds it tends towards a second and higher maximum value, possibly in the neighbourhood of 180 cycles per minute. At points along the pipe beyond 18 metres from the piston the first crest in the curve is absent, but there is in all cases a rapid increase of pressure at about 150 cycles per minute. This indication of the presence of a second peak value probably represents the pressure conditions with fair accuracy, although the actual values of pressure, as already stated, are somewhat uncertain owing to the difficulties associated with the measurement of fluctuating pressure at high speeds. It is reasonable to suppose that

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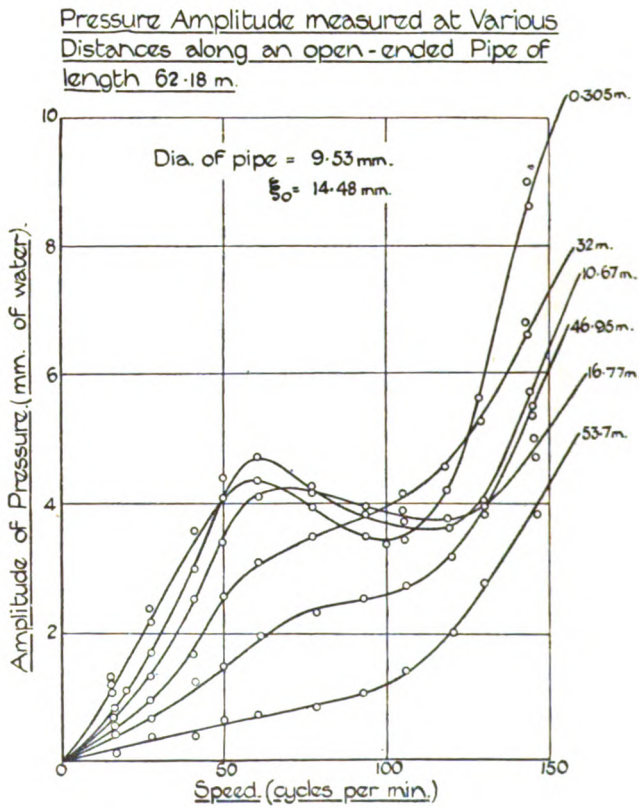
these peak values indicate resonance between the applied motion and the natural vibrations in the pipe; the one at 60 cycles appears to correspond to the fundamental, and the second at 180 to the first overtone. Theoretically, in a frictionless fluid, the pressure should reach infinity simultaneously at all points along the pipe, and the

Fig. 8.



extent to which this rule is violated in practice is evidence of the influence of viscosity in modifying the motion of air in the pipe. The unexpected result that the pressure at 180 cycles is greater than that at 60 cycles has not been satisfactorily explained.

From a consideration of the frequencies and pipe-lengths at which resonance occurs it is possible to form a rough estimate of the velocity of wave propagation. Calculations

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of this velocity have been made from the observed results given in Table III., in fig. 5, and in the following Table, which refers to observations of displacement made by means of a soap-film at the end of 9·53 mm. bore pipes of various lengths, the frequency being maintained constant at 150 cycles per minute :—

TABLE IV.

Length of Pipe (m.).	Amplitude of Displacement. (mm.).
3·05	13·0
15·24	21·2
24·38	29·2 (max.)
30·48	21·2
45·72	10·8
60·96	8·4

The values for the velocity of wave propagation obtained from the conditions of resonance observed during measurements of *displacement* receive an interesting confirmation from a similar value obtained by a consideration of the resonance conditions indicated by the *pressure* curves of fig. 8. The calculations are approximate only, and the simple equation

$$\xi = A \sin (nt - qx) + A \sin \{nt - q(2l - x)\},$$

from which viscosity terms are omitted, has been deemed sufficiently accurate for the present comparison. In the following Table references are given to the sources from which the wave velocities are determined ; the velocities refer to pipes of 9·53 mm. bore in all cases:—

TABLE V.

Velocity of Wave Propagation. (m. per sec.)	Frequency at Resonance. (cycles per minute.)	Resonance Observation.
228	150	From displacement : Table III.
234	115	,, ,, : Table IV.
229	75	,, ,, : fig. 5.
249	60	From pressure : fig. 8.

In the determination of the last value in this table, a mean figure of 60 cycles per minute has been taken for the frequency at which resonance occurs.

From a few measurements of displacement at the end

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of a pipe of 4·75 mm. bore, a velocity of propagation amounting to 59 m. per second is obtained. It may be concluded, therefore, that in general the velocity of wave propagation diminishes rapidly with reduction of pipe diameter; but within the limits of experimental accuracy no appreciable effect of frequency on that velocity can be detected.

In conclusion it may be stated that the present paper is not intended to provide a theory of the transmission of air-waves through pipes. It aims at no more than a comparison of existing theories with the results of experiment. The investigations completed up to the present serve to illustrate a few of the more serious sources of error met with in full-scale work, and indicate the necessity for the introduction into such work of more refined apparatus than has hitherto been employed; for whilst the general problem of viscous flow in pipes may not be insoluble, it remains probable that the difficulty of determining and expressing with mathematical exactness the complex terminal conditions likely to be encountered in the practical measurement of fluctuating pressures, will prove to be greater than that of making use of forms of apparatus in which long transmission pipes are not constituent parts. The essential features of such apparatus appear to be a gauge of very small internal volume and very light moving parts, situated at the point where the fluctuating pressure exists, and an electrical method of transmitting the pressure reading to a central station.

Finally, the writers desire to acknowledge their indebtedness to Mr. R. V. Southwell for his helpful criticism and advice and to Mr. A. H. Bell for his assistance during the early part of the experimental investigation.

LIX. *On the Combined Vibration of a Bar and String, and the "Wolf-Note" of a Stringed Instrument.* By W. B. Morton, *M.A.*, *and* Florence M. Chambers, *M.Sc.*, *Queen's University, Belfast* *.

1. *Introduction.*

THE small motion of the ends of a vibrating string plays an important part in the action of a stringed instrument, inasmuch as it is the link by which the energy is

* Communicated by the Authors.

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transferred to the body, and so to the air. In general, the effect of this yielding of the supports on the pitch is only slight, but it is well known that in instruments of the violin family the interaction of string and body is such that it makes impossible the steady production of one particular note, the so-called "wolf-note."

The late Lord Rayleigh * treated the matter in a general way by supposing that the string was fastened at each end to a mass which was acted upon by a spring, idealizing in this way the inertia and elasticity of the body of an instrument on which the string is stretched. The system made up of the mass and spring has a natural frequency of its own. The effect of the yielding of the ends is to raise or lower the pitch of a note according as it is higher or lower than this critical pitch—in other words, the pitch of the string moves away from that of the supporting system. A further discussion on similar lines is included in Prof. Raman's important monograph on the motion of strings †.

By way of supplementing and illustrating this general method of treatment, it appears of some interest to examine a definite special case in which the motion can be worked out in detail. The case of a string stretched along a uniform bar suggests itself as a rough model or simplification of a stringed instrument. On theoretical grounds also it is interesting to study the coupling together of two elastic bodies which, taken separately, obey such entirely different laws of vibration. The investigation, undertaken with this general point of view, led to a result which seemed to have a possible bearing on the phenomenon of the wolf-note.

2. *Theory.*

A string and bar are joined at their ends by short transverse connecting pieces of negligible mass. Let origins be taken at the centre of each, and let the transverse displacements of string and bar be denoted by y, η respectively. For simple harmonic oscillations of frequency $p/2\pi$ the form of the string is given by

$$y = \mathrm{A}\cos qx + \mathrm{B}\sin qx,$$

where the periodic factor is omitted, and

$$q^2 = p^2 m/l\mathrm{T},$$

m, l, T being mass, length, and tension of the string.

* 'Text-book of Sound,' vol. i. p. 135.

† "Indian Association for Cultivation of Science," Bulletin 15, p. 119.

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The tension of the string will produce a permanent thrust in the bar of the same constant magnitude to a first approximation. We must, in the first instance, take account of this thrust in considering the vibrations of the bar, though it will appear later that its effect on the frequencies is small. Accordingly, the differential equation satisfied by the curve of the bar is

$$\frac{d^4\eta}{dx^4} + 2s^2\frac{d^2\eta}{dx^2} = r^4\eta,$$

where

$$2s^2 = \mathrm{T/EI},$$
$$r^4 = p^2\mathrm{M}/l\mathrm{EI},$$

M, E, I being mass, Young's modulus, and moment of inertia of cross-section.

The general solution is

$$\eta = \alpha\cos r_1x + \beta\sin r_1x + \gamma\cosh r_2x + \delta\sinh r_2x,$$

where

$$r_1^2 = (r^4 + s^4)^{\frac{1}{2}} + s^2,$$
$$r_2^2 = (r^4 + s^4)^{\frac{1}{2}} - s^2.$$

The conditions to be satisfied at the ends $x = \pm\frac{1}{2}l$ are

(1) Equality of displacements, $\eta = y$;

(2) Vanishing of bending moment, $d^2\eta/dx^2 = 0$;

(3) Equality of shear in the bar and the component of the tension transverse to the bar,

$$\mathrm{EI}\, d^3\eta/dx^3 = \mathrm{T}(dy/dx - d\eta/dx).$$

We write

$$\tfrac{1}{2}ql = \theta, \qquad \tfrac{1}{2}rl = \phi,$$
$$\tfrac{1}{2}r_1l = \phi_1, \qquad \tfrac{1}{2}r_2l = \phi_2.$$

The terminal conditions give

(1) $$\alpha\cos\phi_1 + \gamma\cosh\phi_2 = \mathrm{A}\cos\theta,$$
$$\beta\sin\phi_1 + \delta\sinh\phi_2 = \mathrm{B}\sin\theta;$$

(2) $$-r_1^2\alpha\cos\phi_1 + r_2^2\gamma\cosh\phi_2 = 0,$$
$$-r_1^2\beta\sin\phi_1 + r_2^2\delta\sinh\phi_2 = 0;$$

(3) After some reduction,

$$r_2\alpha\sin\phi_1 + r_1\gamma\sinh\phi_2 = -\mathrm{T}q\mathrm{A}\sin\theta/\mathrm{EI}r^2,$$
$$r_2\beta\cos\phi_1 - r_1\delta\cosh\phi_2 = -\mathrm{T}q\mathrm{B}\cos\theta/\mathrm{EI}r^2.$$

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The constants A, α, γ which belong to the even modes of vibration are separated from B, β, δ of the odd modes.

At this stage it is necessary to examine the way in which the unknown quantity p occurs in the magnitudes which have been introduced, and to separate it out from the constants of the problem. It enters in the first power in θ, and so we may take θ as representing the frequency of a note given by the system. In fact, the wave-length in the string is $\pi l/\theta$, so that the pitch of the note is determined when θ is known along with the physical constants of the string. For the fundamental of the string, vibrating with fixed ends, $\theta = \frac{1}{2}\pi$.

The quantity ϕ involves $p^{\frac{1}{2}}$, so θ/ϕ^2 is a constant, viz., $2(m\mathrm{EI}/\mathrm{MT}l^2)^{\frac{1}{4}}$; we denote it by c. In connexion with the third terminal condition, the quantity $\mathrm{T}q/\mathrm{EI}r^3$ comes into the analysis. This contains $p^{-\frac{1}{2}}$; we put it $= k/2\phi$, where $k = (m\mathrm{T}l^2/\mathrm{MEI})^{\frac{1}{2}}$.

The two constants c, k admit of simple expression in terms of two others which have immediate physical meaning. In the investigation of the motion of such a coupled system one would expect to find as determining factors the ratio of the masses of the two members and the ratio of their elasticities or stiffnesses. For the latter we may take, in the present case, the ratio which the tension of the string bears to the force EI/l^2 determined by the bar, being $1/\pi^2$ of the minimum force capable of buckling the bar. Accordingly we put

$$\mu = m/\mathrm{M} \text{ (mass ratio)},$$
$$\epsilon = \mathrm{T}l^2/\mathrm{EI} \text{ (stiffness ratio)}.$$

Then
$$c = 2(\mu/\epsilon)^{\frac{1}{4}},$$
$$k = (\mu\epsilon)^{\frac{1}{2}}.$$

An immediate acoustical significance can be attached to the quantity c. Multiplied by a certain number it gives the interval-ratio between a definite proper pitch of the string and a definite proper pitch of the bar. Here, and afterwards, when string and bar-pitches are mentioned, it is supposed that the string has fixed ends and the bar has free ends. If we take the fundamental pitches in both cases we have, for the string,

$$\theta = \tfrac{1}{2}\pi,$$
$$p = \pi(\mathrm{T}/ml)^{\frac{1}{2}};$$

for the bar,
$$\phi = 3\pi/4 \text{ approximately},$$
$$p = 9\pi^2(\mathrm{EI})^{\frac{1}{2}}/4(\mathrm{M}l^3)^{\frac{1}{2}}.$$

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So (bar-frequency)/(string-frequency)

$$=9\pi(m\mathrm{EI})^{\frac{1}{2}}/4(\mathrm{MT}l^2)^{\frac{1}{2}},$$
$$=9\pi c/8.$$

Under ordinary circumstances k is small, while c may have any magnitude.

Returning now to the determining equations (1), (2), (3), we eliminate the arbitrary constants and obtain "period-equations" for the even and odd vibrations in the rather complicated forms—

Even :

$$\phi(\rho_2^3 \tan \phi_1 + \rho_1^3 \tanh \phi_2) = -k \tan \theta (1+\sigma^4)^{\frac{1}{2}}.$$

Odd :

$$\phi(\rho_2^3 \cot \phi_1 - \rho_1^3 \coth \phi_2) = -k \cot \theta (1+\sigma^4)^{\frac{1}{2}}.$$

In these we have written

$$\rho_1 = r_1/r,$$
$$\rho_2 = r_2/r,$$
$$\sigma = s/r;$$

so that

$$\rho_1^2 = (1+\sigma^4)^{\frac{1}{2}} + \sigma^2,$$
$$\rho_2^2 = (1+\sigma^4)^{\frac{1}{2}} - \sigma^2.$$

We have $\rho_1\rho_2 = 1$, but both symbols are retained for the sake of symmetry.

An interesting way of checking the accuracy of the analysis in this and similar questions is to verify that the angular momentum of the system, as it passes through the centre of the swing, is zero. For even modes this is ensured by the symmetry on the two sides of the centre; but for an odd mode it implies the vanishing of the angular momentum for half the bar and string taken together. The expression of this reduces to the equation

$$\int_0^{\frac{1}{2}l} (\mathrm{M}\eta + my)x\,dx = 0;$$

putting

$$y = \mathrm{B} \sin qx,$$
$$\eta = \beta \sin r_1 x + \delta \sinh r_2 x,$$

we get

$$\mathrm{M}\{\beta(\sin \phi_1 - \phi_1 \cos \phi_1)/r_1^2 - \delta(\sinh \phi_2 - \phi_2 \cosh \phi_2)/r_2^2\}$$
$$+ m\mathrm{B}(\sin \theta - \theta \cos \theta)/q^2 = 0.$$

When the values of β, δ given by the first and second

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terminal conditions are put in, this reduces to the period-equation.

The equations as they stand are quite intractable, since p, which is sought, occurs in ρ_1, ρ_2, σ as well as in θ, ϕ, ϕ_1, ϕ_2. A great simplification is effected if σ^2 can be neglected in comparison with unity, and under ordinary conditions this is the case. On putting in the values it will be found that

$$\sigma^2 = k/4\theta\ ;$$

k is a small fraction, while θ, in the most interesting cases, is near a multiple of $\frac{1}{2}\pi$, corresponding to a pitch given by the string. If σ^2 is neglected, ρ_1, ρ_2 become unity and $\phi_1 = \phi_2 = \phi$. We thus obtain—

Even modes:

$$\phi(\tan\phi + \tanh\phi) = -k\tan\theta\ ;$$

Odd modes:

$$\phi(\cot\phi - \coth\phi) = -k\cot\theta,$$

with

$$\theta = c\phi^2.$$

The two constants c, k (or μ, ϵ) determine the distribution of the proper pitches of the combined system, *i.e.* the ratios of their frequencies. Having obtained a pair of values of $\theta\phi$ satisfying these equations, we can express the forms of string and bar by the equations—

Even:

$$y = \mathrm{A}\cos\frac{2x\theta}{l}\Big/\cos\theta,$$

$$\eta = \tfrac{1}{2}\mathrm{A}\left\{\cos\frac{2x\phi}{l}\Big/\cos\phi + \cosh\frac{2x\phi}{l}\Big/\cosh\phi\right\}.$$

Odd:

$$y = \mathrm{B}\sin\frac{2x\theta}{l}\Big/\sin\theta,$$

$$\eta = \tfrac{1}{2}\mathrm{B}\left\{\sin\frac{2x\phi}{l}\Big/\sin\phi + \sinh\frac{2x\phi}{l}\Big/\sinh\phi\right\}.$$

When k vanishes the equations break up into those which give the vibrations of a string with fixed ends and a free-free bar separately, viz.,

Even: $\tan\phi + \tanh\phi = 0$, $\tan\theta = \infty$.

Odd: $\cot\phi - \coth\phi = 0$, $\cot\theta = \infty$.

In the above analysis the usual practice has been followed of neglecting the effect of the rotatory inertia of the bar.

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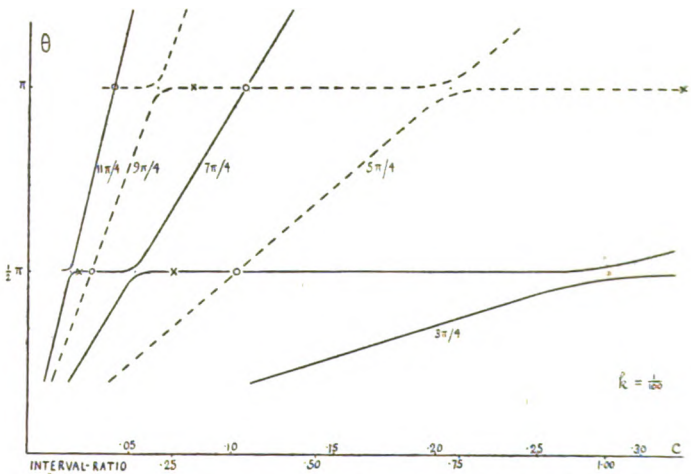
Before proceeding to the discussion of the simplified period-equation, it is worth while to compare the small influence which the neglected term has upon the frequency with that exerted by the thrust in the bar. To take the rotation of the sections into account the term $\frac{Mp^2}{AlE}\frac{\partial^2\eta}{\partial x^2}$ has to be added to the differential equation already discussed. Here A is the area of the cross-section. The effect is merely to change the meaning of the coefficient $2s^2$, and to add to σ^2 a term which reduces to $(2\kappa^2\phi^2/l^2)$, where κ is the radius of gyration of the section. The ratio of this to the former σ^2 is $(4\kappa^2\theta^2/l^2\mu)$. Here the small quantity $\mu=m/M$ in the denominator counteracts the smallness of κ^2/l^2, so the two small effects may be comparable in magnitude.

Fig. 1.



To examine the solutions of the period-equation for the combined system as simplified, we assume a definite value for the constant k. Then for each value of ϕ we can calculate θ, and thence $c=\theta/\phi^2$. The results are shown by plotting θ against c. On the diagram are drawn a series of lines radiating from the origin, $\theta/c=\phi^2$, for values of ϕ in odd multiples of $\pi/4$. The values $3\pi/4$, $7\pi/4$, etc., correspond very nearly to the even modes of vibration of the bar by itself, and $5\pi/4$, $9\pi/4$, etc., to the odd modes.

The diagram (fig. 1) has been drawn for $k=\cdot01$. The even and odd modes are indicated by full and broken lines respectively. When a vertical is drawn through the proper

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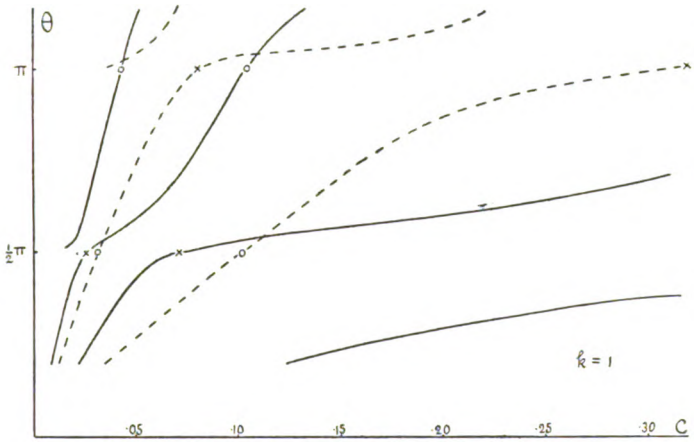
value of c, it meets the various branches at heights proportional to the frequencies of the notes given by the compound system. It will be seen that in general these consist of string-notes slightly modified by the yielding of the ends of the bar and bar-notes modified by the presence of the string. With this value of k the divergences are inappreciable, except near the gaps, where the bar-lines run off into string-lines. For clearer illustration of the course of the curves the exaggerated fig. 2 has been drawn for $k=1$. The graduations marked below the axis give the interval-ratio $9\pi c/8$.

Fig. 2.



The curves fall to the origin in a succession of cascades. The falls have the approximate direction of the radiating lines which represent the undisturbed frequencies of the bar, and run from a gap in one string-level to a gap in the next level of the same kind (even or odd). The intermediate level of the other kind is crossed at points marked with a circle. After the fall the curve runs inwards close to the horizontal line, crossing it at a point marked with a cross and dropping in another fall from the next gap.

The curves are not carried down to the origin, to indicate that the simplified equations lose their significance for small values of θ when σ^2 ceases to be negligible. For this reason a branch, belonging to the odd equation, along which θ and ϕ are small, is omitted. It would indicate a mode of vibration, having a single node at the centre, which is mechanically impossible. There is no physical interest to justify an

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examination of the way in which the origin is approached by the exact curves. As θ approaches zero the quantity ρ_1 becomes infinite, so the terms $\tan\phi_1$ and $\cot\phi_1$ introduce essential singularities.

There are three kinds of special points to be considered, viz., those in the centre of the gaps and the points marked with a circle and with a cross. The first and second are alike cases of resonance, when there is coincidence between a bar-note and a string-note, but the two are distinguished by quite different effects:—

(1) At the gaps the coincident notes correspond to bar and string vibrations which are of the same kind—both even or both odd. Such a pitch cannot be elicited from the combined system. In place of it there are two displaced pitches, producing "resonance with beats." When the bar and string frequencies coincide exactly the number of beats is a minimum; mistuning in either direction makes them come faster.

To examine this analytically we take the even equation,

$$\tan\theta = -\phi\,(\tan\phi + \tanh\phi)/k.$$

When k is small the right-hand side is in general large, and θ lies near an odd multiple of $\pi/2$. If $\delta\theta$ is the displacement of the proper pitch of the string,

$$\delta\theta = k/\phi\,(\tan\phi + \tanh\phi),$$

with $\phi = (\theta/c)^{\frac{1}{2}}$, the approximate value being put for θ. This approximation fails if c is such that the value $\theta = (2n+1)\dfrac{\pi}{2}$ makes $(\tan\phi + \tanh\phi)$ a small quantity; in other words, when this value of θ nearly corresponds to an even mode of the bar also. We know that even in this case, for small k, the deviation from the undisturbed string-frequency is small, so we may write

$$\phi(\tan\phi + \tanh\phi) = \phi(\sec^2\phi + \operatorname{sech}^2\phi)\delta\phi$$
$$= (\sec^2\phi + \operatorname{sech}^2\phi)\delta\theta/2c,$$

which gives

$$\delta\theta = 2ck/(\sec^2\phi + \operatorname{sech}^2\phi)\delta\theta,$$
$$\delta\theta = \pm\{2ck/(\sec^2\phi + \operatorname{sech}^2\phi)\}^{\frac{1}{2}}.$$

Here ϕ has one of the values lying close to $3\pi/4$, $7\pi/4$, etc., so as an approximation we may neglect $\operatorname{sech}\phi$ and put $\sec^2\phi = 2$, giving

$$\delta\theta = \pm(ck)^{\frac{1}{2}} = \pm(2m/\mathrm{M})^{\frac{1}{2}} \text{ approximately.}$$

The same result is arrived at for the odd modes.

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When the fundamentals of bar and string coincide,

$$\theta = \pi/2. \qquad \phi = 3\pi/4, \qquad c = \theta/\phi^2 = 8/9\pi.$$

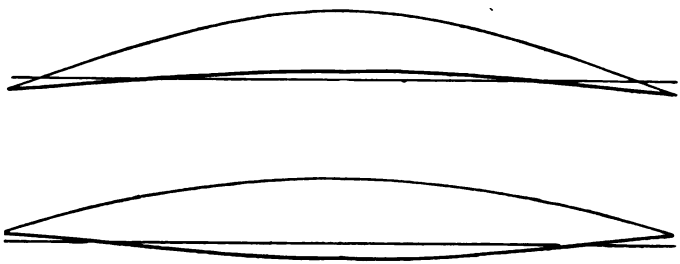
For $k = \cdot 01$ this gives

$$\delta\theta = \pm \cdot 05 \text{ roughly,}$$
$$= 3^\circ \text{ say.}$$

This agrees with measurement made on the graph.

The forms of bar and string are shown on an exaggerated scale on fig. 3, with $\delta\theta = \pm 10^\circ$, $\theta = 90^\circ$.

Fig. 3.



(2) When an even frequency of the string coincides with an odd frequency of the bar, or *vice versa*, the note is given unaltered by the combination; for the period-equations are satisfied, for any value of k, if we have at the same time $\tan\theta = 0$ and $\tan\theta + \tanh\phi = 0$ or $\cot\theta = 0$ and $\cot\theta - \coth\phi = 0$.

The corresponding points are marked with a circle. They are the intersections of the level $\theta = \frac{\pi}{2}$ with the lines

$$\phi = 5\pi/4 \quad \text{at} \quad c = 8/25\pi = \cdot 102$$

and

$$\phi = 9\pi/4 \quad \text{at} \quad c = 8/81\pi = \cdot 031,$$

and of $\theta = \pi$ with

$$\phi = 3\pi/4 \quad \text{at} \quad c = 8/9\pi = \cdot 283$$

and

$$\phi = 7\pi/4 \quad \text{at} \quad c = 8/49\pi = \cdot 052.$$

Here, and elsewhere, the approximate values are taken for ϕ.

In this motion the bar vibrates as if it were alone; the string has loops at its ends instead of nodes, so that an even

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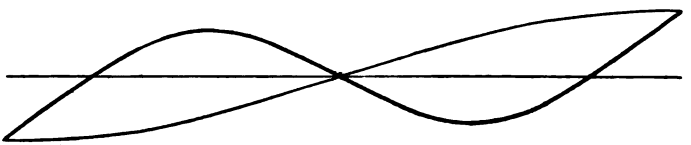
mode is changed into an odd one having the same wave-length in the string (fig. 4). The string exerts no influence on the vibration of the bar because the tensions at the ends have no transverse component. It is to be noted that, for the same values of k and c, there is another mode of vibration, with a very slightly higher pitch, in which the string vibrates with its ends almost motionless. The raising of the pitch implies shortening of the wave-length, so that the nodes fall a little inside the ends of the string. On the graph for

Fig. 4.



$k = \cdot 01$ the point which represents this node is indistinguishable from that marked with a circle; the separation can be seen on fig. 2. Since the energy of the motion is conveyed to the air by the bar, this second note will be scarcely audible in comparison with the other. Under ordinary conditions the two notes will, in any case, be too close to give beats, and also a very small displacement, in the direction of increasing c, brings us to the intersection of the bar and string curves, with complete fusion of the two frequencies and disappearance of beats. Therefore this kind of resonance may be called "resonance without beats," to distinguish it from that indicated by the gaps in the curves.

(3) In the motion just discussed, a natural pitch of the string when vibrating with fixed ends is yielded by the combined system. There is another case in which this occurs, when the ends of the string actually are fixed points. The period-equations are satisfied when both sides become infinite, which happens if, for a particular value of c, we have at the same time

$$\text{(Even mode)} \qquad \tan\theta = \infty, \qquad \tan\phi = \infty,$$

$$\text{(Odd mode)} \qquad \cot\theta = \infty, \qquad \cot\phi = \infty.$$

Confining attention to the fundamental of the string,

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$\theta = \frac{1}{2}\pi$, this pitch is given unaltered if, along with this,

$$\phi = \pi/2, \quad 3\pi/2, \quad 5\pi/2, \text{ etc.,}$$

i. e. if

$$c = 2/\pi, \quad 2/9\pi, \quad 2/25\pi, \text{ etc.,}$$

$$= \cdot 637, \quad \cdot 071, \quad \cdot 025.$$

The corresponding points on the diagram are marked with a cross.

The form of the string is now $y = A \cos \pi x/l$, so the ends are nodes. Equation (2) shows that the constant γ vanishes, the hyperbolic term disappears from the equation of the bar, and it also vibrates in a sine-curve. The relation between the amplitudes of the string and bar-curves is given by the third terminal conditions

$$\alpha/A = -k \sin \theta/2\phi \sin \phi$$

$$= -k/\pi, \quad k/3\pi, \quad -k/5\pi,$$

$$= -\mu, \quad 3\mu, \quad -5\mu, \ldots$$

since $ck = 2\mu$.

The tangents to the string and bar at the motionless ends always slope on opposite sides of the horizontal (fig. 5).

Fig. 5.

Similarly, the first overtone of the string is given unaltered with motionless ends when

$$\theta = \pi,$$

$$\phi = \pi, \quad 2\pi, \quad 3\pi, \ldots$$

and

$$c = 1/\pi, \quad 1/4\pi, \quad 1/9\pi \ldots$$

$$= \cdot 319, \quad \cdot 080, \quad \cdot 036.$$

3. *Experiments.*

In order to test the theory some experiments were made, the "bar" being a piece of light metal tubing such as is used for a kind of gong. It was a little over a centimetre in diameter and 54 cm. long. On this a steel pianoforte wire of

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29 S.W.G. was mounted in the following manner. At one end of the tube a coned brass sleeve was inserted transversely, and into this fitted a conical brass peg with a cross-piece. At the other end a slit was made along the diameter of the tube parallel to the axis of the peg, and a small bridge was soldered to the tube above this. A knot was made on the wire, which was then slipped into the slit, drawn tightly over the bridge, and passed through a hole in the peg. By means of the peg the string could be tuned to any desired pitch and held by friction of peg against sleeve. The range of tension was such that either the first or second overtone of the string could be brought into coincidence with the first overtone of the bar. The system was suspended horizontally, with the string underneath, by cords attached to the outer nodes of the bar in this (odd) mode of vibration.

The system was kept in forced oscillation by the action of periodic force applied by a small electromagnet, through which passed the alternating current from a triode valve. The frequency of this was altered by means of a variable inductance in the circuit.

The natural frequencies of the system are indicated by maximum response.

The various pitches were expressed in terms of the corresponding lengths of a standard sonometer wire. The alternating current from the valve passes through this wire, which runs between the poles of a strong electromagnet, fed with a steady current. The reaction between the alternating valve-current and the field gave rise to a periodic force on the sonometer wire The length of wire giving maximum resonance is inversely proportional to the frequency of the alternations.

After a frequency of the combined system had been determined in this manner, for a definite tension of the wire, the bar was clamped and the measurement repeated so as to get the corresponding string-pitch with fixed ends. The length of sonometer wire corresponding to the bar-pitch used was found by the method of beats.

The following effects were observed:—

(1) When the string and bar-pitches are not close together a large visible motion of the string was obtained at the proper frequency of the applied force, but only a very faint sound was heard. The motion of the ends of the string is now very small, and its proper pitch very slightly displaced.

(2) When the pitch of the second (even) overtone of the string is approaching that of the first (odd) overtone of the bar the amplitude of the string motion decreases, but the

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note becomes louder. When the pitches coincide there is no visible movement of the string while a loud sound is produced by the bar. The string has a node at the centre, loops at the ends and at the points of trisection. This is the case of "resonance without beats."

(3) When the first overtone of the string (odd) is near the first overtone of the bar (odd) there are two different frequencies of the applied force which produce loud sounds. As the string-pitch approaches the bar-pitch from below, the upper of the two resonances rises from the bar-pitch. When the coincidence is exact the two resonances are at equal distances above and below the common pitch of string and bar. As the string-pitch rises higher the lower resonance approaches the bar-pitch from below. The observed amplitude of the string-motion is large, being maximum when coincidence is exact. This case of "resonance with beats" was examined quantitatively in the manner explained above, the lengths of sonometer wire being determined for the resonance-pitches and the string-pitch for a series of tensions of the wire. The first and second lengths are then plotted against the third.

For a theoretical graph to compare with these measurements we cannot use the representation of fig. 1. in which k is constant and the independent variable is c. This has to be modified so that $\mu = \frac{1}{2}kc$ is constant. For the coincidence of the pitches in question we have

$$\theta = \pi, \qquad \phi = 5\pi/4, \qquad c = 16/25\pi = \cdot 2037.$$

The experiments therefore cover ranges of $c\phi$ extending on the two sides of these values.

The equation to be satisfied is

$$\phi(\coth\phi - \cot\phi) = k\cot c\phi^2.$$

For a series of values of c running from ·190 to ·230 the corresponding values of $k = 2\mu/c$ were calculated. For the bar and string used in the experiments $\mu = m/M = \cdot 00317$. Then the set of curves $y = k\cot cx^2$ was drawn along with the curve $y = x(\coth x - \cot x)$ for the range of x between ·210 and ·240. The intersections give the values of ϕ for each c. The resonance frequencies are proportional to ϕ^2 and the string-frequency is inversely as c. The length of the sonometer wire corresponding to the bar-note was 34·4 cm. Accordingly the magnitudes plotted in the experimental graph are got by calculating

$$34\cdot 4 \times c/\cdot 2037 \quad \text{and} \quad 34\cdot 4 \times (225)^2/\phi^2.$$

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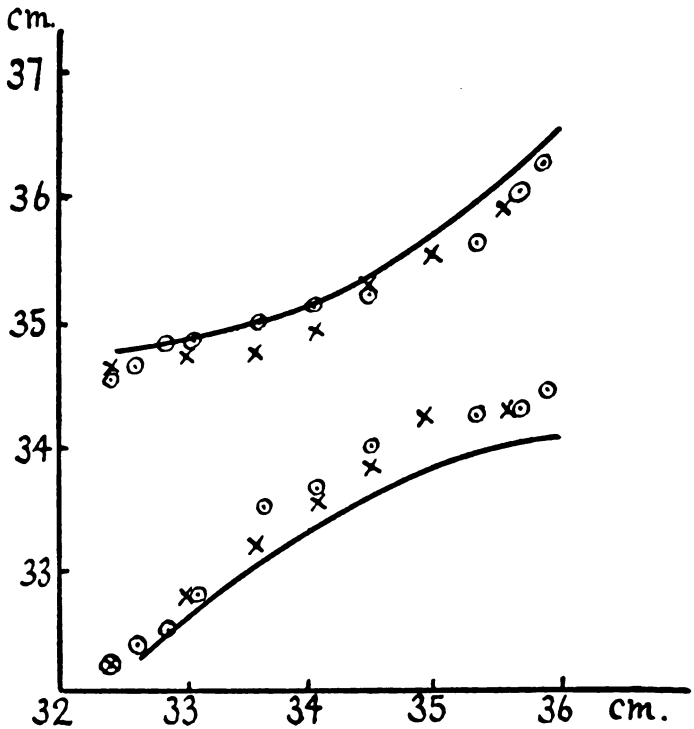
The result is shown in fig. 6. The readings obtained in two series of experiments are shown marked with a circle and a cross respectively.

Fig. 6.



4. *Wolf-Note.*

It remains to consider the possible bearing of the above theory on the curious phenomenon of the "wolf-note." It is generally agreed that the difficulty in producing this note is due to its coinciding with a proper pitch of the body of the instrument, a kind of resonance not to be confused with the resonance of the enclosed mass of air, as investigated by Helmholtz. Assuming this, we have first to inquire which of the two kinds of resonance is more likely to be concerned. The question is not easy to decide *à priori*, and it seems possible that resonance of either kind might produce the effect. Consider first that without beats. Here there is

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a possibility of a sudden change in the mode of vibration of the string at the critical frequency, passing from the normal manner in which the motion is large in the centre and small at the ends to the type of fig. 4, with the middle point of the string at rest and the ends moving largely. One would expect such a transition to upset the ordinary technique of bowing and to prevent the bow from biting properly. On the other hand, under the forcing action of the bow the formation of the central node may in actual fact be prevented, and so the normal mode of vibration be retained.

The other kind of resonance is more in accordance with the fluctuating nature of the motion, as shown in the photographic records taken first by White and afterwards by Raman *. The displacement-time curves for points on the string and belly are like those given by two beating vibrations. White regarded the fluctuations as beats between a natural frequency and that impressed on the instrument by the bow. Raman pointed out that such beats of forced vibrations would occur only at the beginning of the action of the applied force, before the establishment of the permanent *régime*. He found the explanation of the fluctuations in his theory of the action of the bow. According to this theory, a bow which presses on the string with a given force and moves with a given velocity can maintain the fundamental vibration only so long as the rate at which energy is withdrawn from the string at its ends remains below a certain limit. When this is exceeded the mode of vibration alters into a type in which the octave predominates. When the wolf-tone is sounded on the string the resonance builds up an exceptionally large motion of the body, accompanied by a rapid withdrawal of energy from the string. Then the mode of vibration changes, resonance ceases, the rate of loss of energy falls below the limit, the normal action of the bow is restored, and the process is repeated in regular cycles.

The plate which accompanies Prof. Raman's paper shows simultaneous traces of the motion of a point on the string and a point on the belly of a violoncello taken by the method used by Prof. Barton and his pupils. Both traces show the periodic changes, each cycle containing about sixteen vibrations. In agreement with the theory, the maxima of the body-movement follow those of the string by about a quarter-period of the cycle, and at the minima the octave harmonic is clearly evident. The string-vibration at the

* White, Proc. Camb. Phil. Soc. xviii. p. 85 (1915); Raman, Phil. Mag. xxxii. p. 391 (1916).

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maxima has the familiar zigzag form. The curve at the minima resembles that which is obtained when the fundamental component is omitted from the harmonic analysis of this form as given by Helmholtz *. The scale of the photograph is too small to permit of an exact verification of this. The vibrations of the body, reproduced on a much larger scale, are rather irregular in appearance, and seem to consist of the fundamental, mainly or altogether, except at the minima where the octave shows up.

One is tempted to connect the beat-like course of the vibrations, as revealed by these photographs, with the two close frequencies shown to exist for the free vibrations of the bar-string system in "resonance with beats." It might be supposed that the fundamental in the Fourier series for the rectilinear form of vibration was replaced by two slightly displaced frequencies, each having half the amplitude and beating together. Beginning in phase with each other, they would build up the zigzag form. When the phase-difference amounted to a half-period they would cancel and give the intermediate form with predominant octave. This appeared plausible, but when the wave-forms were plotted by calculation on this basis, for comparison with the observed trace, it was found that the rectilinear forms returned only after *two* periods of the beats. The reason is that at the first return of maximum amplitude of the combined vibration the phase is reversed in relation to the remaining terms of the harmonic series. The displacement

$$\sin 2\pi n_1 t + \sin 2\pi n_2 t$$

$$= 2 \cos \pi(n_1 - n_2)t \,.\, \sin \pi(n_1 + n_2)t$$

has its amplitude

$$= 2 \quad \text{for } t = 0,$$

but $$= -2 \quad \text{for } t = 1/(n_1 - n_2).$$

If in the graph of the resultant displacement we measure from a crest at one maximum to a crest at the next we shall find the distance to differ by a half wave-length from an integral number of waves. Thus the distance between the recurrences of the rectilinear vibration-forms for the string should be twice that between the maxima for the fundamental vibrations of the body, whereas these distances are equal on the photograph.

* 'Sensations of Tone' (Ellis), Appendix VI. p. 384.

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The phenomenon of "resonance with beats" cannot therefore be invoked as an explanation of the observed cyclical phenomena at the wolf-pitch, and we are left with Prof. Raman's theory, which relies solely on considerations of energy-transfer, and makes no reference to modes of vibration of the combined system of string and body. It is possible that the ignoring of frictional forces in our theory has deprived it of any applicability to the actual case of a stringed instrument, but it is difficult to think that there is no connexion between a note which does not exist as a free vibration, in the one instance, and a note which is difficult to produce as a forced vibration in the other.

There is one observation recorded in Raman's paper which seems to indicate the existence of the two different kinds of resonance. The effect of a mute attached to the bridge was examined, and was found to be a lowering of the pitch of the wolf-note. A load of 40·4 gms. was found to depress the frequency from 176 to 137, and also to cause "two new but comparatively feeble resonance-points to appear at 100 and 184 respectively, without any attendant cyclical phenomena."

Raman has also published * a photograph of the motion of string and bridge when the 'cello is played pizzicato at the wolf-note pitch. This is a case of a free vibration, but the damping is so great that any cyclical character which the motion might possess could not readily be detected on the graph. The amplitude of the string-motion is greatest just after the release, while that of the bridge rises to a maximum after five or six vibrations; but this lag is conditioned, in part at any rate, by the fact that we are dealing with the beginning of the motion when the "initial conditions" still influence the form.

One or two fresh points in connexion with the wolf-note phenomenon were suggested by some observations made at our request by Mr. L. McCann, B.Sc., who is a skilled violin-player. On the only violin on which he could find a wolf-note this lay high up on the E string, at the pitch B, a twelfth above the note of the open string. When the tension of the string was relaxed the wolf was still found at the same pitch, *i. e.* with a shortened string. When the open pitch of the string was brought down to C, the exceptional character of the note B began to disappear, and was quite gone at B flat.

The constancy of the wolf-note pitch agrees with the idea

* 'Nature,' vol. ci. p. 264 (1918)

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that it corresponds to a proper pitch of the body of the violin, but there are two points difficult to explain. The first arises from the high frequency of the note, about 1980. This cannot be the fundamental pitch of the body. If it is an overtone, why is the wolf-effect not found on the lower proper pitches?

We made an attempt to determine roughly the proper pitches of a violin, regarded as a bar of variable mass-distribution, using the method given by Lord Rayleigh for such a case ('Sound,' vol. i. pp. 114 & 291). We were encouraged to try this by the successful application of the method by T. C. Tobin to calculate the proper periods of large ships *. We used the tabulated values of the functions involved which are given in his paper. The use of the same mathematical machinery to deal with a liner or a violin is a rather striking instance of the unimportance of the linear scale. The values found were as follows:—

	First approximation.	Second approximation.
Fundamental	464	455
First overtone.....	1289	1236
Second overtone.....	2526	2454

This leaves it doubtful whether the wolf-note found by Mr. McCann was the first or second overtone. It is to be remembered that our measurements were made on a different violin.

The other point is the disappearance of the wolf-note with the lowered tension of the string. This may perhaps be explained on Raman's theory if we suppose the decreased force between string and body implies a smaller transference of energy at the ends. On the other hand, it involves also a shortening of the string and a consequent decrease of the ratio m/M, causing the gaps on our graph to close up.

In the hope of obtaining fresh light on some of the points raised in this section, we intend to try the experimental method described in the second part of this paper to find the proper periods of a violin which has a marked wolf-note.

* Inst. of Naval Architects, Paper No. 6 (1922).

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LX. *The Electrical Conductivity of some Dilute Liquid Amalgams.* By E. J. WILLIAMS, *M.Sc., Late University Research Student at University College, Swansea* *.

OBSERVATIONS on the electrical conductivity of amalgams have been made by various workers, notably Larsen †, Weber ‡, and Matthiesen and Vogt §. The problem has been considered theoretically by Skaupy ‖, who has made use of the experimental results obtained by the above-mentioned observers. The variation of the relative conductivity with temperature, and the nature of the departure of the variation of the relative conductivity with concentration from a linear law, are quantities of considerable theoretical interest, and in order to obtain reliable values of these it is necessary to have accurate and comprehensive data. The observations which have been referred to include only a few made at temperatures higher than 100° C., whilst the results for the lower temperatures due to different observers are not always in agreement. The object of the present work was to provide accurate data covering a greater range of temperature, and to extend observations to amalgams of metals not previously investigated. This paper ¶ mainly deals with the experimental results obtained in the case of cadmium amalgams, which had been previously investigated by several observers **, and also in the case of magnesium and indium amalgams, which had received no attention previously ††.

For the sake of comparison with the amalgams and also for testing the accuracy of the experimental method, the electrical conductivity of pure mercury was measured over the range 0° C. to 300° C.

* Communicated by Prof. E. J. Evans, University College of Swansea.

† *Ann. Physik*, (4) i. p. 127 (1900).

‡ *Wied Ann.* xxiii. p. 471 (1884).

§ Phil. Mag. xxiii. p. 161 (1862).

‖ *Deutsch. Phys. Gesell. Verh.* xviii. p. 252; *Phys. Zeits.* p. 597 (1920).

¶ The observations are being continued by another worker.

** Larsen, *Ann. der Physik*, (4) i. p. 127 (1900); Weber, *Wied. Ann.* xxiii. p. 471 (1884); Calvo, *Ion*, ii. p. 408 (1910); Borneman & Rauschenplatt, *Metallurgie*, ix. pp. 473 & 505 (1912); E. von Schweidler, *Sitzber. Akad. Wien*, civ. p 278 (1895); A. Battelli, *Atti Accad. Lincei*, (4) iv. p. 206 (1887); R. S. Willows, Phil. Mag. [5] xlviii. p. 445 (1899); Vicentini a Cattaneo, *Atti Accad. Fisicritici*, (4) lxv. pp. 147, 227 (1893).

†† Willows (Phil. Mag. [5] xlviii. (1899)) made observations on the conductivity of an amalgam containing 1 per cent. of magnesium, but as the amalgam was in the solid state it does not concern us.

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Experimental Arrangement.

The resistance was measured by means of a Callendar and Griffiths Bridge, which when used in conjunction with a delicate galvanometer enabled the resistance to be measured with an accuracy of ·0001 ohm, this corresponding to a tenth of a millimetre of the bridge-wire. Nothing would be gained by determining the resistance with greater accuracy, since ·0001 ohm corresponded to the change of resista c· produced by the smallest change of temperature measurable in these experiments. The various resistances of the bridge were calibrated in terms of the largest resistance by the usual method. A knowledge of the absolute values of the resistances of the bridge was not necessary for determining the relative change of the resistance of an amalgam due to change of temperature or composition. It was, however, necessary that the various resistances of the bridge should be consistent amongst themselves, which was ensured by the calibration.

The resistance to be measured was connected to the bridge by flexible leads about two yards long, and compensating leads, connected to terminals provided for them on the bridge, were used to avoid effects produced by changes of resistance of the leads during the periods of making measurements.

The amalgam was contained in a capillary tube which opened out into two vertical limbs as shown in fig. 1 *a*. Into these limbs fitted the leads as shown in fig. 1 *b*.

The copper wire *c* was connected to the bridge, and also to the amalgam in the capillary by means of the mercury *m* and the platinum wire *p*. The copper wire was kept in a fixed position by means of a capillary *b* in order that the resistance of the leads be maintained constant during measurements. In making a determination of resistance, the resistance with the leads in the same amalgam cup was first measured and then with the leads in the limbs of the capillary tube. The difference between the two resistances was the difference between the resistances of two columns of amalgam at the same temperature t; the resistance of the leads cancelling out. The two columns referred to are the column between the platinum terminals when in the same amalgam cup, and that between them when in the limbs of the capillary. The former is of course almost negligible in comparison with the latter, but this need not be assumed. In all the measurements these two columns were the same, so that the difference between their resistances, or what will

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be henceforth called the resistance of the amalgam, was proportional to the resistivity at that temperature *.

For measurement of resistance at 0° C. a bath containing melting ice was used, and for measurement at room temperature a water bath. At all higher temperatures the amalgam columns were immersed in a boiling liquid; the agitation of the liquid caused by boiling ensuring a uniform temperature. The following is a list of the liquids used with their respective approximate boiling-points in °C.:—water (100), alcohol (129), aniline (184), diethyl aniline (221), eugenol (256), glycerine (288), diphenylamine (300). Some of the liquids did not boil at a constant temperature with continued heating, the temperature increasing gradually as they

Fig. 1 *a*.

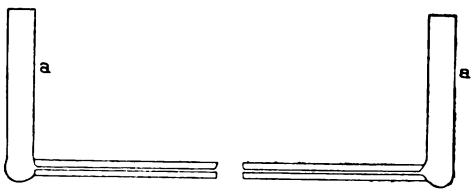
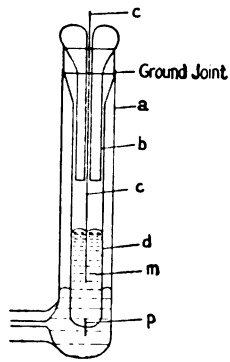


Fig. 1 *b*.



were boiled. In those cases, the observations were not made until the rate of variation of temperature became sufficiently small to warrant an accurate determination of resistance and temperature. The time taken by the capillary tube and amalgam to assume the temperature of the bath was inappreciable and caused no trouble. In all cases, however, a series of readings of temperatures and resistances was made to ensure a reliable result.

Two thermometers were used to determine the temperature; the one a platinum thermometer and the other a mercury thermometer. A set of mercury thermometers graduated in tenths of a degree and certified by the National Physical Laboratory was used. The difference between the temperatures recorded by the two thermometers respectively

* This statement applies to the relation between the resistivity and the resistance of the amalgam when the latter is corrected for the expansion of the capillary tube.

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did not in general exceed 0°·2 C. and when the difference was greater it was probably due to disuniformity in the temperature of the bath.

One of the difficulties met with was the formation of bubbles in the capillary tube at the higher temperatures. There was greater tendency for this to happen in tubes of small diameter, and at the higher temperatures tubes of narrow bore (diameter $<$ ·7 mm.) were not used. This formation of bubbles could be avoided to a large extent by heating the amalgam to a temperature not far from its boiling-point before and after adding it to the capillary tube, and in the latter case removing any bubbles that formed. If after an experiment no bubbles were present in the tube it could be assumed that none had formed at the high

Fig. 2.

temperature, and therefore that the result obtained was free from any uncertainty arising from this effect. The values of the resistivity at high temperatures obtained by some observers are high compared with those obtained in the present experiments, and probably the discrepancy arises from the formation of bubbles in the tubes used by these observers.

Magnesium amalgams readily oxidized when exposed to the air, and in order to prevent this oxidation, magnesium amalgams were prepared and added to the capillary tube in a vacuum, the entire process being carried out in a sealed glass tube shown in fig. 2. The mercury was added at *a*, and the magnesium at *b*, the magnesium falling into the side vessel *c* and kept separated from the mercury. The tube was then evacuated and the open ends *a* and *b* sealed. The mercury was then poured into vessel *c* on to the magnesium,

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and the amalgam prepared. The amalgam was then poured back into the capillary tube and the resistance measurements made. The resistance of the leads could not be eliminated exactly as before because the platinum lead *d* could not be detached and put in the same cup with *e*. An extra lead *f* was therefore provided near the lead *e*, the ratio of the effective resistance of *f* to that of *d* and *e* being determined by preliminary observations at room temperature.

Variation of the Resistance of Pure Mercury with Temperature within the range 0°–300° C.

Two series of observations were made, one with a capillary tube (A) of diameter 0·5 mm. giving a resistance of the mercury of about 1·7 ohms at room temperature, the other with a tube (B) of diameter ·7 mm. and giving a resistance of the mercury column of ·8 ohm. The results are given in Table I.

α_t=average temp. coeff. from 0° to t°, i.e., $\frac{r-r_0}{r_0 t}$;

α_c=average temp. coeff. from 0° to t° corrected for expansion of the glass tube *;

ρ_t and σ_t are the values of the resistivity and conductivity respectively at t°, the conductivity at 0° C. being, by definition of unit resistance, 10630.

TABLE I.

Temperature t.	$\alpha_t \times 10^4$.			$\alpha_c \times 10^4$.	$\rho_t \times 10^9$.	$\sigma_t \times 10$.
	With Tube A.	With Tube B.	Weighted Mean.			
0° C.					94074	106300
16·8	8·99	8·97	8·983	9·066	95507	104705
100	9·772	9·760	9·768	9·861	103351	96758
129	10·064	10·077	10·068	10·169	106415	93972
184	10·622	10·614	10·619	10·734	112655	88766
221	10·999	11·000	10·999	11·121	117194	85329
256	11·395	11·390	11·393	11·521	121820	82086
288		11·716	11·716	11·853	126188	79245
297		11·824	11·824	11·964	127509	78423

* The values of the linear expansion coefficient were determined for the glass capillary tube used, for different ranges of temperature. It increased with the temperature, the observed value for the range 0°–100° being $8{\cdot}6 \times 10^{-6}$, and for the range 0°–180°, $9{\cdot}6 \times 10^{-6}$.

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The estimated probable error in α (excluding the room temperature value) is on the average about ·15 per cent. The difference between the values of α_t obtained with tubes A and B respectively is nowhere greater than this. Various formulæ have been proposed to represent the variation of the resistivity of mercury with temperature. The values of the resistivity at different temperatures obtained in the present experiments can be represented by a quadratic formula to within 0·5 per cent. This deviation is, however, greater than the experimental error, the estimated probable value of which is about 0·02 per cent. By introducing a cubic term into the formula the resistivity can be represented with a maximum deviation of only ·025 per cent. and an average deviation of ·015 per cent. The formula is :

$$\rho_t = \rho_0\{1 + \cdot 0_3 8879\, t + \cdot 0_6 975\, t^2 + \cdot 0_9 20\, t^3\} \quad . \quad . \quad (1)$$

A very accurate determination of the resistivity at 100° relative to that at 0° has been made by Jager and Steinwehr *. The value of the resistivity at 100° given by the above formula agrees to within ·01 per cent. with their value. The only previous data that have been found for temperatures above 100° are due to Vicentini and Omodei †, and Benoit ‡. The values of the temperature coefficient obtained by the former for the ranges 0°–100° and 0°–300° are about ·7 per cent. greater than those obtained here, whilst for ranges from 0° to intermediate temperatures the values given are about 2 per cent. greater. The values of the temperature coefficient obtained by Benoit are on the whole about 2 per cent. less.

Conductivity of Amalgams.

The results of the observations on the amalgams of cadmium, indium, and magnesium are given in Table II. A brief discussion of the results, which will also serve to explain the table, will now be given.

Cadmium Amalgams.

Two specimens of cadmium were used, one obtained from Harrington, London, and the other from Kahlbaum, Germany. The resistances of amalgams of equal concentrations prepared from each of these specimens were found to be the same to within experimental error.

* *Ann. d. Physik*, (4) xliii. p. 1165 (1914).
† *Atti Accad. Torino*, xxv. p. 30 (1889).
‡ *Comptes Rendus*, lxxvi. p. 341 (1873).

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The values of the conductivity changes at room temperature for concentrations ranging from ·009 per cent. to 4 per cent. are given in the first part of Table II. p is the weight of cadmium per unit weight of amalgam, δ is the relative increase of conductivity, that is,

$$\frac{\text{conductivity of amalgam} - \text{conductivity of mercury at the same temp.,}}{\text{conductivity of mercury}}$$

and a is the estimated rate of variation of the relative increase of conductivity with concentration at infinite dilution.

The values of b in column 6 measure the departure of the variation of the conductivity with concentration from a linear law. The constancy of b (the variations are within experimental error for amalgams containing less than 2 per cent. of cadmium) shows that the variation of the conductivity of dilute amalgams with p obeys a quadratic law, the conductivity, c, of an amalgam of concentration p being given by

$$c = c_0\{1 + 7{\cdot}80\,p - 20\,p^2\}.$$

Skaupy, as the result of an analysis of Larsen's results, concludes that the variation of the conductivity of dilute cadmium amalgams deviates considerably from a quadratic law. Except for very weak amalgams the values of m, $= \frac{\delta}{p}$, obtained in the present experiments and those obtained by Larsen agree to within about 0·5 per cent. The weakest amalgam investigated by Larsen contained ·0163 per cent. of cadmium, and the value of m obtained for this was 9·8, which marked a sudden increase over the values obtained for the higher concentrations. There is no evidence whatever in the present results of the existence of such an increase in m. Regarding as real this sudden increase Skaupy estimated $\underset{p=0}{\mathrm{Lt}}\ m$ as 10·8, and as a result could not represent the conductivity by a quadratic formula.

The results obtained at different temperatures show that the relative increase of conductivity, δ, increases uniformly with the temperature, the percentage increase being independent of the concentration of the amalgam to within experimental error. The actual magnitude of the increase with temperature is comparatively small, the increase in δ due to an increase of temperature from 0° to 300° C. being only 20 per cent. of its value at 0° C. Bornemann and Rauschenplatt* have made observations on the conductivity of dilute

* *Loc. cit.*

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cadmium amalgams at high temperatures, and they give results for two amalgams whose concentrations expressed in atoms per cent. are 0·99 and 3·02 respectively. The ratio of the values of δ at 100°, 200°, and 300° calculated from these results is 1·00 : 1·07 : 1·00. The ratio according to the results obtained in the present experiments is 1·00 : 1·06 : 1·14.

Indium Amalgams.

Indium was found to pass readily into solution in mercury. Two different specimens of the metal were used, and were found to give the same results to within experimental error. Owing to the limited supply of the metal, amalgams containing more than 3 per cent. of indium were not investigated, and only a limited number of amalgams of lower concentrations could be used.

It is seen from the table that the variation of m with concentration is small, and the value of b is consequently uncertain. The relative increase of conductivity increases with the temperature, and as in the case of cadmium amalgams, the percentage increase is independent of concentration. The increase is greater than for cadmium amalgams, the percentage increase due to an increase of temperature from 0° to 100° being 8 for indium amalgams as compared with 4 for cadmium amalgams.

Magnesium Amalgams.

Magnesium in the form of ribbon was used. Although the metal dissolved in mercury at ordinary temperatures, the rate of dissolution was greatly increased by warming the mercury. If prepared in the presence of air the magnesium was not retained in the amalgam; the resistance of the filtered liquid being the same as that of pure mercury. This was due to the rapid and complete oxidation of the magnesium contained in the amalgam, an effect which had been previously noticed by many observers. This oxidation was prevented by employing a method which has already been described in the account of the experimental arrangement.

It was found that on cooling an amalgam containing 0·2654 per cent. of magnesium, the conductivity increased suddenly at about 4° C and then continued to increase irregularly. The variations were attributed to the separating out of solid from solution, and an examination of the amalgam showed the presence of solid floating on the surface. It was concluded, therefore, that an amalgam containing 0·2654 per cent. of magnesium is saturated at 4° C.

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In consequence of this comparatively small "magnesium content" of mercury, only three amalgams were investigated. The change of conductivity was, however, so great that accurate measurements could be made.

Relative increase of Conductivity and Atomic Concentration of the Metal.

In the last column of Table II. are given the values of the ratio of the relative increase of conductivity at infinite dilution to the concentrations expressed in atoms of the metal per atom of mercury. Skaupy* has found that this quantity, A, is approximately the same for amalgams of different metals. This conclusion means that atom for atom the effects of different metals on the conductivity of mercury are the same. The results which have been obtained in this investigation for indium and magnesium amalgams are new, and were therefore not included amongst those considered by Skaupy. It is therefore interesting to find that the values of A for cadmium and indium respectively are very nearly the same; the values at room temperature being in the ratio 1 : 0·95. A for magnesium is somewhat high in comparison, being 41 per cent. greater than A for cadmium. It is worth noticing, however, that weight for weight there is not the slightest trace of equivalence between the effects of cadmium and magnesium upon the conductivity of mercury; the respective values being in the ratio 1 : 6·5.

The variation with temperature is small and is in the same direction for the three metals, and consequently the relative values of A do not change much with temperature. The ratio $A_{Cd} : A_{In} : A_{Mg}$ at 184° C. is 1 : 1·02 : 1·41 as compared with 1 : 0·95 : 1·41 at 14° C.

Summary of Results.

The values obtained for the resistivity of mercury at various temperatures within the range 0°–300° C. are represented by the formula

$$\rho_t = \rho_0\{1 + \cdot 0_3 8879t + \cdot 0_6 975t^2 + \cdot 0_9 20t^3\}$$

to within the probable experimental error, the estimated value of which is ·02 per cent. The resistivity at 100° C. according to this formula differs only by ·01 per cent. from a determination made by Jager and Steinwehr (1914).

The results obtained for cadmium amalgams show that the

* *Loc. cit.*

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TABLE II.

Nature of Amalgam.	Temp. °C.	Conc., p, $\times 10^2$.	$\delta \times 10^2$.	$m = \frac{\delta}{p}$.	$\frac{a-m}{p} = b$	a = Lt. m. $p=0$	A.
Cadmium Amalgams.	14°	·0087	·06$_9$	8		7·80	4·37
		·0437	·33$_8$	8			
		·0654	·51$_3$	7·8			
		·1129	·87$_8$	7·7$_8$	2×10		
		·2742	2·13$_0$	7·7$_6$	$1\frac{1}{2}$×10		
		·4379	3·36$_9$	7·6$_9$	$2\frac{1}{2}$×10		
		·7152	5·45$_9$	7·6$_3$	24		
		·9825	7·45$_7$	7·59	21		
		·9913	7·54	7·60	20		
		1·4741	11·05	7·50	20		
		1·9608	14·50	7·40	20		
		2·9566	21·49	7·27	18		
		3·8423	27·36	7·12	$17\frac{1}{2}$		
	100°	·505	4·05	8·0	$2\frac{1}{2}$×10	8·12	4·58
		·728	5·77	7·9$_3$	$2\frac{1}{2}$×10		
		·9913	7·84	7·92	20		
		1·9608	15·09	7·70	21		
		2·9566	22·47	7·59	18		
		3·8423	28·51	7·43	18		
	0°	·9913	7·49	7·56		7·76	4·35
	184°	·9913	8·27	8·35		8·55	4·80
	302°	·9913	9·00	9·09		9·29	5·22
Indium Amalgams	14°	·107	·75	7·0		7·20	4·14
		·498	3·51	7·0$_4$			
		1·062	7·56	7·12			
		1·845	13·19	7·15			
		1·933	13·74	7·12			
		3·043	21·30	7·00			
	100°	·498	3·80	7·60		7·75	4·45
		1·062	8·13	7·65			
		1·933	14·84	7·67			
		3·043	22·96	7·55			
	0°	1·933	13·60	7·05		7·13	4·10
	184°	1·933	16·30	8·44		8·52	4·90
Magnesium Amalgams.	14°	·0524	2·65	50·7		50·7	6·18
		·1181	5·93	50·2			
		·2654	13·18	49·7			
	100°	·1181	6·23	52·8		53·3	6·51
		·2654	13·96	52·7			
	0°	·1181	5·88	49·8		50·3	6·14
	3°·8	·2654	13·08	49·3		50·3	6·14
	184°	·2654	15·08	54·6		55·6	6·78

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conductivity of dilute amalgams (containing < 2 per cent. Cd) can be represented to within experimental error by a quadratic formula, the relative conductivity at 14° C. of an amalgam containing p parts of Cd in 1 part of amalgam being given by $1+7{\cdot}80\,p-20\,p^2$. The departure of the variation of the conductivity of indium amalgams with concentration from a linear relationship is small, whilst in the case of magnesium amalgams it could not be accurately tested as amalgams containing about $\frac{1}{4}$ per cent. of magnesium are saturated at room temperature. The estimated values of a, $= \underset{p\to 0}{\mathrm{Lt}}\ \frac{c-c_0}{c_0\cdot p}$, where c is the conductivity of an amalgam of concentration p at 14° C. and c_0 is the conductivity of pure mercury at the same temperature, for indium and magnesium amalgams respectively are 7·20 and 50·7, as compared with 7·80 for cadmium amalgams.

The effects of these metals, atom for atom, upon the conductivity of pure mercury are sensibly the same, a result in agreement with an empirical relation obtained by Skaupy as the result of consideration of amalgams of other metals (including cadmium, however). The values of A, $= \underset{p'=0}{\mathrm{Lt}}\ \frac{c-c_0}{c_0\cdot p'}$, where p' is the atomic concentration, for Cd, In, and Mg respectively, are 4·37, 4·14, and 6·18.

Results are given showing the effect of temperature upon the conductivity of Cd amalgams over the range 0°–300° C. and of In and Mg amalgams over the range 0°–184° C. The change of relative increase of conductivity with temperature is small, the values of $\frac{a_{(100°)}}{a_{(0°)}}$ for Cd, In, and Mg amalgams being 1·041, 1·077, and 1·060 respectively, the relative increase being independent of the concentration to within experimental error. As a result of the smallness of the temperature effect, the extent of the agreement with Skaupy's rule is very little affected by considering values of conductivity at different temperatures. The ratio of the values of A_{Cd}, A_{In}, A_{Mg}, which relate to values of conductivity at 184° C., is 1 : 1·02 : 1·41 as compared with the value 1 : 0·95 : 1·41 of the ratio of the values relating to room temperature conductivities.

In conclusion I wish to express my warm thanks to Professor E. J. Evans for his most valuable assistance during the course of the work.

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LXI. *The Electric Charge carried by Thorium X and Thorium Emanation Recoil Atoms in Gases.* By G. H. Briggs, *B.Sc., Lecturer in Physics in the University of Sydney* *.

THE charge carried by recoil atoms, resulting from the decay of the radio-active emanations when the latter are mixed with a gas, has been the subject of numerous investigations. Wellish † was the first to show definitely that the recoil atoms of radium active deposit at the end of their recoil path in air, hydrogen, and carbon dioxide are either positively charged or neutral. In two papers ‡ the writer has described experiments by which values were found for the percentage of the recoil atoms positively charged at the end of their recoil paths in various gases, for Ra A recoiling from Ra Em and Ra B from Ra A. It was shown also that the behaviour of the active deposit of Th Em in an electric field is explained, if it is assumed that in any gas the percentage of Th A atoms positively charged at the end of their recoil path is the same as for Ra A, and that a similar relation holds for Th B and Ra B. This similarity in the behaviour of isotopic atoms also gave a satisfactory explanation of Lucian's § results for the active deposit of Actinium emanation. It is probable that the recoil atom during its recoil path through the gas captures and loses electrons in much the same manner as positive rays and α particles do, and that the final charged state at the end of the recoil path is a matter of chance, depending on the nature of the collisions near the end of the path and not on the initial velocity of the recoil atom. Identical results would not be found for isotopic recoil atoms if the charge at the end of the recoil path were dependent on the initial velocity. The present paper describes experiments in which Th X and Th Em were examined from the same point of view.

Part I.—*Thorium X.*

Two very simple methods of preparing sources which give appreciable amounts of Th X by recoil were tried and proved satisfactory:—(*a*) A platinum disk, diameter 2 cm., was platinized just sufficiently to produce a slight tarnish, and a small quantity of mesothorium bromide dissolved in water

* Communicated by Sir E. Rutherford, F.R.S.
† Phil. Mag. xxviii. p. 417 (1914).
‡ Phil. Mag. xli. p. 357 (1921); P. Roy. Soc. N.S.W. lvii. 249 (1923).
§ Phil. Mag. xxviii. p. 761 (1914).

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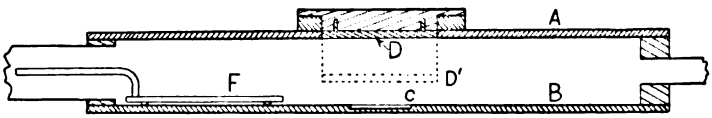
was spread over the surface and allowed to dry. (*b*) Radiothorium was separated in the usual way from mesothorium, the precipitate carrying down the radiothorium being allowed to settle on a similar platinum disk. The gamma-ray activity of the former source was equivalent to that of 0·15 mg. radium and the latter to that of 0·10 mg. Both of these sources gave Th X, and also Th A and Th B by recoil. These products were readily collected on a negatively charged electrode, an exposure of one minute giving sufficient Th X to be easily measured with a Dolazalek electrometer having a sensitivity of a few hundred millimetres per volt. It will be shown later, however, that the efficiency of recoil was only about 3 per cent.

The exposure apparatus consisted of a box, shown in longitudinal section in fig. 1, made of two brass plates A and B separated by ebonite. Its internal dimensions were

Fig. 1.



16 × 4·3 × 2 cm. The source C was placed in a recess so that it was flush with the bottom of the box, and the recoil atoms were collected on a circular brass plate D, which in some experiments was flush with A, and in others, when in the position D′, was only 7 mm. from B. The time of activation of the plate D was controlled by moving with an electromagnet a slider F which covered the source. To carry off Th Em escaping from the latter, a current of the gas under test was maintained through the box at a mean velocity of about three centimetres per second. The gases were dried with phosphorus pentoxide and filtered. In order to obtain saturation of the recoil atoms more readily in the presence of the intense ionization from the source, the working pressure was always maintained in the neighbourhood of 10 cms. Voltages up to 1200 were used; the time of exposure was generally 15 or 20 minutes. The activated disks were covered after removal with thin aluminium foil to prevent the escape of Th Em produced by the decay of the Thorium X collected, and their α-ray activities were measured at various times during the next 6 or 10 days. Often a series of exposures were made, using the gas and air alternately. The order of making the exposures did not influence

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the result in any definite manner, although there was sometimes difficulty in obtaining values consistent to within less than 2 per cent.

The percentage of Th X positively charged in air was found by making exposures in which the source and the disk to be activated were separated by only 0·4 mm. and the pressure was reduced to 0·005 mm. Under these conditions all the atoms recoiling from the source should strike the disk. The ratio of the amount of Th X collected in this way to the amount collected in air in an equal time at a pressure of 10 cm., the distance between the source and the disk D being 7 mm. and the voltage 400, was found in successive experiments to be 100·0, 100·2, and 99·4 per cent. It is concluded therefore, that in air all the Th X recoil atoms are positively charged at the end of their recoil paths.

The experimental results obtained by comparing the amount of Th X collected in various gases with that collected in air are given in the second column of Table I. The third column gives the electric force.

TABLE I.

Gas.	Ratio of the amount of Th X collected in gas to the amount collected in air × 100.	Electric force in volts per cm.
Helium	99·9	600
Oxygen	101	530
Hydrogen	100·2	600
Nitrogen	100·0	530
Carbon dioxide	99·7	600
Nitrous oxide	99	600
Acetylene	101	400
Ammonia	94·6	530
Ethyl ether	94·7	600
Methyl acetate	94	800
Ethyl acetate	94	800
Acetone	90	800
Methylal	87	570
Hexane	90	500

In these experiments the ionization from the source is very intense, saturation of the ions being obtained in air at

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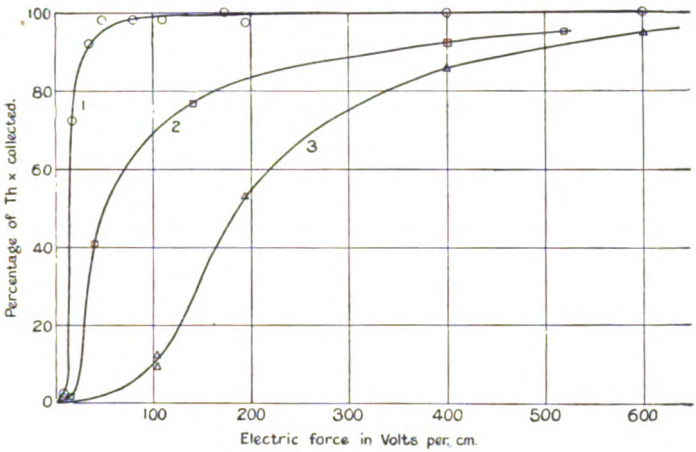
atmospheric pressure only with an electric force of 250 volts per cm. In fig. 2 are curves showing how the amount of Th X collected on the upper plate varied with the electric force in the case of air and ammonia at 12 cm. pressure and in ethyl ether at 10 cm. pressure. It is seen that saturation of the Th X atoms is much more difficult to obtain in ammonia than in air and more difficult still in ether. From the upward trend of the curves for ether and ammonia it appears that at sufficiently high voltages they would coincide with that for air. This is probably true for all the other

Fig. 2.



Saturation curves for Thorium X recoil atoms in :

1. Air.
2. Ammonia.
3. Ethyl ether.

gases or vapours which give experimental results below 100 per cent. The experiments had to be discontinued before this point could be more thoroughly investigated, but it seems fairly safe to conclude that not only in the first seven gases of Table I., where the values differ from 100 per cent. by less than the experimental error, but also in ammonia and all the vapours investigated the Th X atoms are all positively charged at the end of the recoil path. This is in marked contrast to the behaviour of Th A and Ra A or Th B and Ra B, as can be seen from Table II., which summarizes the results of the present experiments and those given in the two previous papers by the author.

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TABLE II.

Percentage of recoil atoms positively charged at end of recoil path.

	Th X.	Th Em.	Ra A and Th A.	Ra B and Th B.
Helium	100		93·7	>96·4
Oxygen	100	Zero	88 *	95 *
Hydrogen	100	Zero	82·4†	93†
Air	100	Zero	82·4	93
Nitrogen	100			
Carbon dioxide	100	Zero	71·8	83·2
Carbon monoxide	...	...	67 *	82 *
Argon	...	...	61·8	81·8
Nitrous oxide	100	...	61·8	79·8
Methane	...	...	15·9	78·1
Acetylene	100	...	2·2	74·9
Ammonia	100	...	Zero	69·4
Ethylene	...	...	,,	61·8
Hydrogen sulphide	...	...	,,	54·9
Ethyl ether	100	...	,,	5·5
Methyl acetate	100	...	,,	5·0
Ethyl acetate	100	...	,,	3·5
Acetone	100	...	,,	4·3
Methylal	100	...	,,	3·7
Hexane	100	...	,,	3·3

* Estimated from value for active deposit of Ra Em, Briggs (*loc. cit.*).
† ,, ,, ,, Wellish (*loc. cit.*).

It may be asked whether these experiments in which the recoil occurs under very unfavourable conditions can yield trustworthy results. This question will be considered in the following sections, which give a more detailed account of the active deposit collected from these sources under various conditions.

Typical decay curves of the deposit collected in various gases are shown in fig. 3. In air the activity reaches a maximum in four hours, and after about six days decays with the period of Th X. The curve shows that in air the activated plate collects from the source a certain amount of Th A or Th B together with the Th X. The less marked maximum in the curve for ammonia shows that the total

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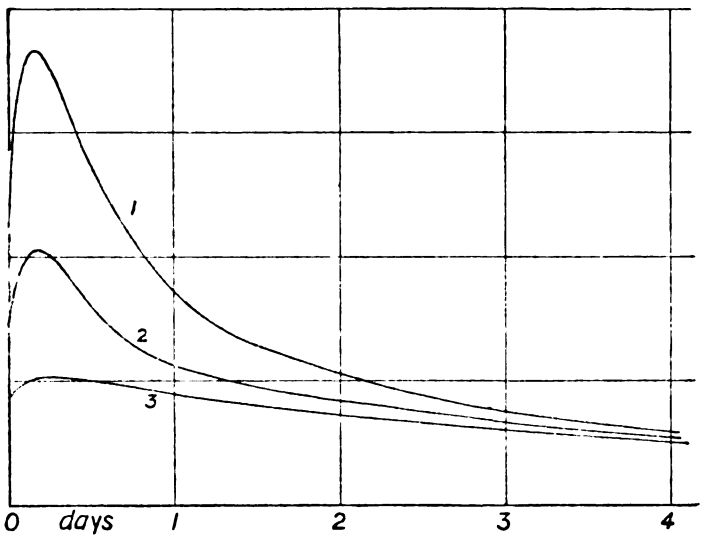
amount of Th A + Th B collected is smaller than in air. In ether hardly any Th A or Th B is collected, and the activity decays almost as if it were due entirely to Th X. There is, however, just enough Th A or Th B present to mask the maximum which would be expected at the end of the first day if only Th X had been collected. Decay curves of this type were found with all the vapours examined.

Fig. 3.



Decay of α-ray activity of the deposit collected in:

1. Air.
2. Ammonia.
3. Ethyl ether.

To determine whether the Th A or Th B collected in air was received through recoil from the source or from the decay of free emanation which has escaped from the source, a sheet of metal was attached to the disk D on the down-stream side and in the same plane. The amount of Th A + Th B collected on this was measured at various distances along it and was found to be practically constant and, for an equal area, about 1 per cent. of the Th A + Th B collected on D. Hence the Th A and Th B collected on the activated disk is practically all due to recoil from the source. It may be noted that when the upper plate was positively charged no detectable activity was collected.

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The efficiency *of recoil from the source.*

An approximate estimate of this quantity was made in the following manner. The total number of α rays emitted per second from the Radiothorium source was determined from the saturation-ionization current produced by it in air. It was assumed that α rays are emitted in equal numbers from the Radio Th, Th X, Th Em, Th A, and Th C present. This assumption neglects any escape of emanation from the source. Knowing the initial ionization current from the Th X collected in a given time, it was deduced that 1·25 per cent. of the total number of Th X atoms produced in the source escape by recoil, so that the actual efficiency of recoil of the Th X was 2·5 per cent. For the mesothorium source the efficiency was 3·5 per cent. It was also calculated from the decay curve that the mean efficiency of recoil of the Th A and Th B is about equal to that of the Th X. Owing to the fact that only a few per cent. of the recoil atoms escape from the plate, the equality which holds between the numbers of the various kinds of atoms transforming per second in the plate if none escaped is not appreciably disturbed as a result of recoil.

From decay curves, such as those shown in fig. 3 for the deposit when collected in air and in ammonia, it is possible to calculate the ratio "r" of the total number of Th A + Th B atoms collected in ammonia to the total number collected in air. Now, if the present method of experiment is justifiable, the ratio r should be able to be predicted from the previous results for Th A and Th B given in Table II., if in addition the ratio "s" of the number of Th B to the number of Th A atoms escaping from the source were known; s is then the ratio of the efficiencies of recoil of Th B and Th A. From Table II. it can be seen, for example, that for ammonia the ratio r should be

$$\frac{s \times 0 + 69{\cdot}4}{s \times 82{\cdot}4 + 93{\cdot}0}.$$

It was impossible to measure s directly.

In Table III. are values of r for some of the gases used in the present experiments and the values calculated from the results previously published for the case when $s = 1$ and for $s = 1{\cdot}8$, which is the value of s giving the best agreement. That it is possible to obtain this agreement for a series of gases, for which the percentage of Th A positively charged ranges from 82 to zero and of Th B from 93 to 70, is sufficient support for the results obtained in the

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present experiments. The value 1·8 for s leads to the conclusion that the efficiencies of recoil of Th X, Th A, Th B in these experiments are as 1 : 0·78 : 1·40 ; the ranges of the α rays producing the recoil are as 1 : 1·16 : 1·31. These values for the efficiency of recoil neglect any escape of emanation. Some rough measurements indicated that about 10 per cent. of the emanation escaped from the source.

TABLE III.

$$\frac{\text{Amount of Th A + Th B collected in gas}}{\text{" " " in air}} \times 100.$$

	Observed.		Calculated for	
		Mean.	$s=1·8$.	$s=1$.
Carbon dioxide.....	87·5			
	85·3			
	93			
	90·5	89·1	887	88·4
Nitrous oxide	83·6			
	85·3			
	80·9	83·3	82·4	80·7
Acetylene	56·7			
	56·0			
	56 0	56·2	55·0	43·8
Ammonia	46·8			
	46·3			
	49·7			
	49·5			
	52·4			
	50·4			
	45·0	48·6	50·1	39 6

The decay curves for ether and the other vapours used show that a small amount of Th A or Th B is collected. From Table II. it is seen that the percentage of Th A positively charged in gases such as H_2S and NH_3 is zero, while the value for Th B is still quite large. It is most

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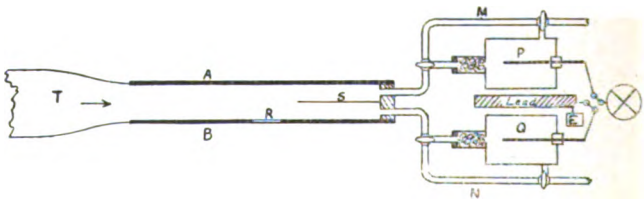
probable therefore that the small amount collected in vapours in the present experiments is wholly due to a small percentage of the Th B recoil atoms being positively charged, while the Th A atoms are all neutral. This is the only conclusion which is consistent with the experiments in ether vapour made by Wellish (*loc. cit.*). He concluded that none of the active deposit of Ra Em was positively charged. However, as Ra B only played a minor part in his experiments, it is readily shown that if 5 per cent. of the Ra B atoms were positively charged in ether they would have produced an effect only of the same order as the experimental error. It is reasonable then to attribute the whole of the Th A + Th B activity collected in the vapours to Th B. In Table II. the percentages of Th B positively charged so obtained are given for the vapours of six liquids. They range from 3·3 per cent. to 5·5 per cent., but are probably not accurate to more than 1 in 5.

Part II.—*Thorium Emanation.*

Having found a method of obtaining Th X by recoil as described in Part I. the charged state at the end of the recoil path of Th Em recoiling from Th X was examined. The apparatus used is shown diagrammatically in fig. 4.

Fig. 4.



The right-hand end of the box AB described in Part I. was divided by a metal diaphragm S parallel to the plates A and B and midway between them. A stream of gas entering through the long tube T was thus divided, one half being led into an ionization chamber P and the other into a similar chamber Q. Either of the ionization chambers could be connected to a quadrant electrometer. When a disk activated with Th X by recoil was placed in the recess R and the plate A charged negatively, it was expected that the emanation atoms

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recoiling from the disk would, if positively charged, travel across to A, give up their charge, and then be swept by the gas stream into the ionization chamber P. If uncharged the emanation atoms would be carried into the ionization chamber Q. To keep the field uniform the diaphragm was always maintained at the mean potential of the plates A and B, and to reduce the disturbing effect of eddies in the gas stream the tube T was about 80 cm. long and 4 cm. in diameter, the section being changed gradually to fit the rectangular end of the box. Some tests with smoke showed that no visible eddies were produced in air. The mean velocity of the gas through the box was generally about 5 to 10 cms. a second and the pressure atmospheric.

The procedure in an experiment was as follows:—A disk activated with Th X was placed in the recess, the electric field in the required direction was established between the plates, and a stream of gas was led through the box and out through the by-passes M and N. The two streams having been adjusted to equality a steady flow was maintained for some time, often more than an hour, and then the streams were allowed to pass through their respective ionization chambers. The ionization current in Q was always very large, and without any added capacity would have given an electrometer rate of 80 mm. a second. By observing the rate of decay on stopping the flow this current was plainly due to Th Em. With air, oxygen, and carbon dioxide no detectable current in P was found. The same result was obtained with various potential differences up to 400 volts with the top plate negative and also when it was positive.

In hydrogen it was found more difficult to get conclusive results. A small ionization current was obtained in P, which was unaltered by reversing the potential or by keeping both plates at the same potential, and was evidentially due to eddies in the gas or to diffusion of neutral emanation atoms from the neighbourhood of the disk into the upper half of the box. By replacing the diaphragm by one about half as long again with a circular aperture 2·5 cm. in diameter directly above the source the ionization current in P was found to be zero.

It appears then that Th Em recoil atoms in air, oxygen, carbon dioxide, and hydrogen are neutral at the end of their recoil paths. This is most probably true of all three radioactive emanations in any gases or vapours, the monatomic gases being perhaps exceptions.

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Summary and Discussion.

A method of obtaining Thorium X by recoil has been described, and the following results for the charged state of Th X recoil atoms have been found.

In He, O_2, H_2, N_2, CO_2, N_2O, and C_2H_2 all the Th X recoil atoms are positively charged at the end of their recoil paths.

In six vapours examined and in NH_3 the percentage of Th X collected on a negatively charged electrode ranged from 87 to 94, and because of the difficulty in the experiments with these of obtaining saturation of the recoil atoms it is concluded that in these also all the Th X atoms are initially positively charged.

The charged state of the Th Em atom recoiling from Th X has been examined in air Au, H_2, O_2, and CO_2, and it is found that in these gases all the recoiling atoms of Th Em are neutral.

The results of an earlier research on Ra A and Th A and Ra B and Th B led to the conclusion as is to be expected that in regard to the charge carried at the end of the recoil path isotopic atoms behave identically. Hence the results obtained apply to corresponding substances in the other radioactive series. Also the results for Ra B should give those for other atoms of atomic number 82 produced by an α-ray change, *i.e.* Ra D, Th D, and Ac D recoiling from Ra C′, Th C′, and Ac C′ and Ra G from Polonium. The result for Th X should give also that for Meso-Th 1 recoiling from Thorium.

The factors which determine the probability of a recoil atom being positively charged or neutral at the end of its recoil path are complex. The recoil atom may be regarded during its passage through the gas as an atom at a high temperature which tends to lose electrons, the degree of ionization approaching an equilibrium state corresponding to the velocity at any instant. As its velocity becomes smaller the degree of ionization on the average becomes less and the recoil atom tends to complete its outer electron group. If we consider the results obtained for the four recoil atoms in any one of the gases investigated, except perhaps helium, there is strong evidence, although observations with Th Em were made only in four gases, that the number of positive recoil atoms is zero for Th Em and 100 per cent. for Th X, with intermediate values for Th A and Th B, the order in which the number increases being Th Em, Th A, Th B, Th X [in some cases Th A is zero as well as Th Em]. On Bohr's scheme the number of

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electrons in the outer groups of these atoms are 8, 6, 4, and 2 respectively, and it is to be expected that a singly or doubly ionized Th X atom will not show a strong tendency to recapture electrons, whereas in the case of Th Em the tendency to revert to the neutral state with the complete group of eight will be marked. The intermediate percentages found for Ra B and Ra A are consistent with this point of view. The ionization potentials of the four atoms increase from about 5·1 for Th X to about 11 for Th Em, but there does not appear to be any reason for expecting the ionization potential to enter into the mechanism in a way that will completely account for the results, in particular that Th X atoms are all ionized, whereas Th Em atoms are all neutral at the end of the recoil path. It appears rather that the results are to be correlated with the chemical properties of the recoil atoms. It is of interest to note here that a similarity between the behaviour of the emanation atom and that of the α particle may be inferred from these experiments and those of Henderson * and Rutherford †, who found that the number of neutral α particles rapidly increases as the velocity becomes less. It is thus probable that the α particle comes to the end of its path as a neutral atom, which is precisely what the present experiments have shown to be the case for the emanation recoil atom.

In the case of either Ra A or Ra B one can examine the influence of the gas on the number of charged recoil atoms. Here the ionization potential of the gas does not seem very important, but, as was pointed out in an earlier paper, the ease of dissociation generally appears to be the dominating factor. Briefly, the hypothesis which was suggested was that at a collision at which the recoil atom dissociates a gas molecule, the recoil particle has a large chance of capturing electrons if positively charged, and at a non-dissociating collision, if its velocity has not fallen below a limiting value, it has a large chance of losing electrons. Thus in a very easily dissociated gas the recoil atom will continue to dissociate when its velocity is too small to ionize itself and the chance of it becoming neutral will be great. This still leaves argon in an anomalous position.

The mechanism is probably further complicated by chemical interaction between the recoil atom and the gas. The recoil atom may form temporary chemical association with some of the products of dissociation. The latter may have been ionized at the collision and when separation

* Proc. Roy. Soc. A, cii. p. 496 (1922).
† Phil. Mag. xlvii. p. 277 (1924).

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takes place the positive charge may remain with the recoil atom. The chance of the recoil atom becoming charged in this fashion should vanish when the velocity of the recoil atom is so small that it has enough energy to dissociate molecules, but not sufficient to ionize as well.

The experiments described in this paper were made in the Physical Laboratory of the University of Sydney. The author is indebted to Professor Vonwiller for his interest during the progress of the work and to Sir E. Rutherford for his helpful criticism of the results.

Cambridge, April 1925.

LXII. *Vibrations of two Pendulums connected by a Spring.* *By* V. N. Solovieff *.

[Plates XVIII.-XX.]

A NUMBER of mechanical models of coupled electric vibrations have been described in the preceding volumes of this Magazine †. The double-cord pendulum of Prof. Barton, so thoroughly investigated in his three valuable papers, seems to be the best of them. It may be also preferred to the other models described in the previous works of Wien, Garbasso, Sellmeier, Oberbeck ‡, etc., as it represents the most ingenious combination as regards simplicity of theory, convenience of construction, and exactness of analogy. Nevertheless, this model scarcely satisfies the above-mentioned natural requests in fullest measure, because Prof. Barton, as well as his numerous predecessors and followers, is trying to imitate the difficult case of *magnetically*-coupled circuits. On the contrary, the case of *electric* coupling, being essentially similar to the practically more important case of inductive coupling, admits an easy mechanical treatment. So perhaps the present paper, in which the author describes a model constructed independently of the works of Prof. Barton (the Philosophical Magazine for 1915–22 was not received in Irkutsk until June 1924), will be of some interest.

The model consists of two high and massive supports,

* Communicated by the Author

† Prof. Barton and Miss Browning, Phil. Mag. xxxiv. p. 246 (1917), xxxv. p. 62 (1918), and xxxvi. p. 36 of the same year; Mr. Jackson, xxxix. p. 294 and xl. p. 329 (1920); A. L. Narayan, xliii. p. 567 (1922).

‡ Wien, *Wied. Annal.* lxi. p. 151 (1897); Garbasso, *Vorlesungen über theoretische Spectroscopie*; Sellmeier, *Pogg. Ann.* cxlv. p. 538 (1872); and Oberbeck, *Wied. Ann.* xxxiv. p. 1041 (1888).

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A and B (fig. 1), of two wooden laths, *a* and *b*, and of two bobs, P and Q, suspended to the laths by means of filaments

Fig. 1.

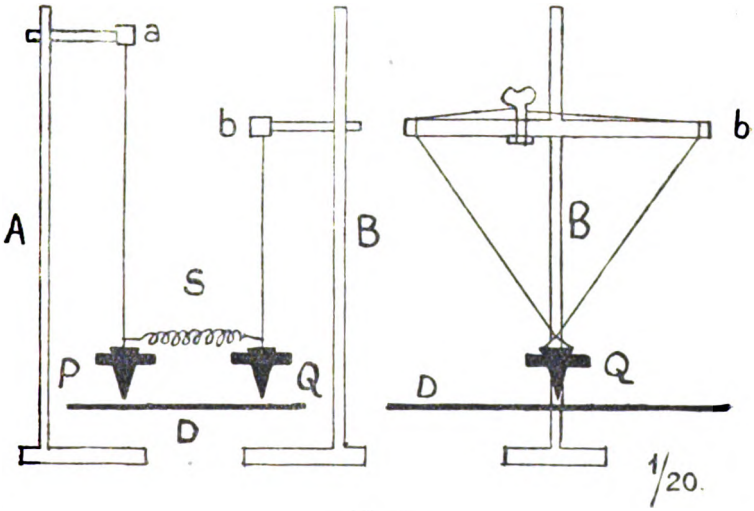
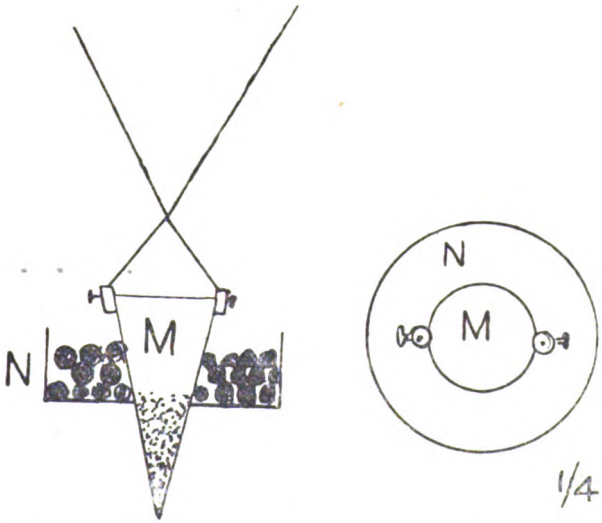


Fig. 2.



or thin wires. Due to such a manner of suspension very good, clear vibrations in the desired plane may be obtained without any difficulty. The bob is represented on fig. 2.

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The tin funnel M is soldered to the cylindrical tub N, made of the same material. The funnels are filled with sand coloured by methylene-blue and the tubs with shot or any substitute. Coupling is performed by means of the spring S, which may be easily replaced. Both bobs are situated in the same horizontal plane, also in the case of different lengths, so that sand traces may be always obtained on a single moving board D. The perspective view of the whole arrangement is shown on Plate XVIII.

Let l_1 and l_2 be lengths, m_1 and m_2 masses, S_1 and S_2 linear displacements of two pendulums P and Q respectively. Further, let k be the extension coefficient of the spring S expressed in $\frac{\text{dynes}}{\text{cm.}}$. Then, neglecting the friction, the differential equations of motion may be written for small oscillations as follows:

$$\left.\begin{aligned} m_1\frac{d^2S_1}{dt^2}+\left(m_1\frac{g}{l_1}+k\right)S_1=kS_2,\\ m_2\frac{d^2S_2}{dt^2}+\left(m_2\frac{g}{l_2}+k\right)S_2=kS_1.\end{aligned}\right\}\quad\ldots\quad(1)$$

Or, putting

$$\frac{k}{m_1}=k_1,\quad \frac{k}{m_2}=k_2,\quad \text{and}\quad \frac{k}{m_1}+\frac{g}{l_1}=P_1^2,\quad \frac{k}{m_2}+\frac{g}{l_2}=P_2^2,$$

which are the frequencies of the first and of the second pendulums *when connected with the spring*, if the second and the first bobs respectively are fastened immovably,

$$\left.\begin{aligned}\frac{d^2S_1}{dt^2}+P_1^2S_1=k_1S_1,\\ \frac{d^2S_2}{dt^2}+P_2^2S_2=k_2S_1.\end{aligned}\right\}\quad\ldots\quad(2)$$

The coefficient of coupling is given by

$$\gamma^2=\frac{k_1k_2}{P_1^2P_2^2}.\quad\ldots\ldots\quad(3)$$

With a corresponding spring (or wire) γ may be increased to 100 per cent.*

* In all the models here described it is practically impossible to obtain the coupling greater than 50–60 per cent.

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Solving the equations (2) in the ordinary way, we obtain the general solution

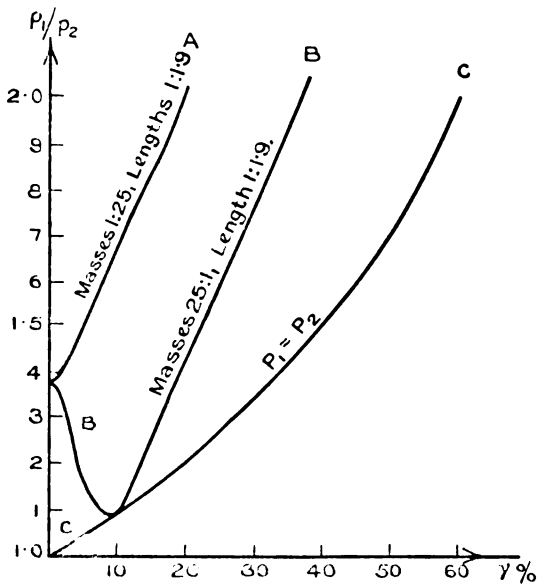
$$\left.\begin{aligned} S_1 &= A_1 \sin(p_1 t + \alpha_1) + A_2 \sin(p_2 t + \alpha_2), \\ S_2 &= \frac{P_1^2 - p_1^2}{k_1} A_1 \sin(p_1 t + \alpha_1) + \frac{P_1^2 - p_1^2}{k_1} A_2 \sin(p_2 t + \alpha_2), \end{aligned}\right\} \quad (4)$$

where A_1, A_2, α_1, α_2 are arbitrary constants and p_1 and p_2 are given by

$$\left.\begin{aligned} 2p_1^2 &= P_1^2 + P_2^2 + \sqrt{(P_1^2 - P_2^2)^2 + 4k_1k_2}, \\ 2p_2^2 &= P_1^2 + P_2^2 - \sqrt{(P_1^2 - P_2^2)^2 + 4k_1k_2}. \end{aligned}\right\} \quad . \quad . \quad (5)$$

The relations among the ratio of frequencies $\frac{p_1}{p_2}$ and γ are graphically represented on fig. 3, showing the difference

Fig. 3.



between the cases when the heavy bob is on the long pendulum (graph A) or on the short one (graph B), just as in the double-cord model*. When $P_1 = P_2$, $\frac{p_1}{p_2}$ may be expressed in terms of γ:

$$\frac{p_1}{p_2} = \sqrt{\frac{1+\gamma}{1-\gamma}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

* Phil. Mag. no. 211, p. 44, July 1918.

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just the same formula as for two magnetically or electrically-coupled circuits with equal periods (graph C).

Introducing the initial conditions in the equations (4) and in the differentiations of these with respect to time, we may find the solution for every special case. But we shall confine ourselves in this paper to the case of a single displacement.

Then for $t = 0$, $s_1 = S_0$, $s_2 = 0$, $\frac{ds_1}{dt} = \frac{ds_2}{dt} = 0$, and the special solution will be

$$\left.\begin{aligned} s_1 &= S_0 \frac{P_1^2 - p_2^2}{p_1^2 - p_2^2} \cos p_1 t - S_0 \frac{P_1^2 - p_1^2}{p_1^2 - p_2^2} \cos p t_2, \\ s_2 &= S_0 \frac{(P_1^2 - p_1^2)(P_1^2 - p_2^2)}{k_1(p_1^2 - p_2^2)} (\cos p_1 t - \cos p_2 t). \end{aligned}\right\} . \quad (7)$$

In the case of resonance ($P_1 = P_2 = P$) these may be rewritten as follows :

$$\left.\begin{aligned} s_1 &= \tfrac{1}{2} S_0 (\cos p_1 t + \cos p_2 t), \\ s_2 &= \tfrac{1}{2} S_0 \sqrt{\frac{m_1}{m_2}} (\cos p_1 t - \cos p_2 t), \end{aligned}\right\} \quad . \quad . \quad (8)$$

where

$$\left.\begin{aligned} p_1^2 &= P^2(1+\gamma) \\ \text{and} \quad p_2^2 &= P^2(1-\gamma) \end{aligned}\right\} . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

When the lengths of pendulums are equal ($l_1 = l_2$) (7) becomes

$$\left.\begin{aligned} s_1 &= \frac{m_2}{m_1 + m_2} s_0 \cos p_1 t + \frac{m_1}{m_1 + m_2} s_0 \cos p_2 t, \\ s_2 &= \frac{m_1}{m_1 + m_2} s_0 (\cos p_1 t - \cos p_2 t), \end{aligned}\right\} . \quad (10)$$

where

$$\left.\begin{aligned} p_1^2 &= P_1^2 + k_2, \\ p_2^2 &= P_2^2 - k_2. \end{aligned}\right\} . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

In the case of electrically-coupled circuits (fig. 4) the equations of motion are in the usual notation :

$$\left.\begin{aligned} L_1 \frac{d^2 l_1}{dt^2} + \left(\frac{1}{C_1} + \frac{1}{C_{12}}\right) l_1 &= \frac{1}{C_{12}} l_2, \\ L_2 \frac{d^2 l_2}{dt^2} + \left(\frac{1}{C_2} + \frac{1}{C_{12}}\right) l_2 &= \frac{1}{C_{12}} l_1. \end{aligned}\right\} . \quad . \quad . \quad (12)$$

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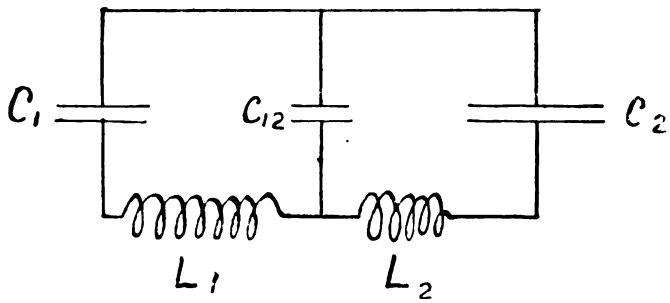
It is clear that these equations are identical with (1). Indeed, the dimensions of the respective coefficients are exactly the same if we put with Prof. Barton the inductances L_1 and L_2 analogous to the masses m_1 and m_2, and the capacities C_1, C_2, C_{12} to the spring factors $\frac{l_1}{m_1 g}$, $\frac{l_2}{m_2 g}$, and $\frac{1}{k}$. $\left(\text{The dimension of } \frac{mg}{l} \text{ is just the same as of } k, \textit{i. e.}, \frac{\text{gr. cm.}}{\text{cm. sec.}^2}\right)$.

Fig. 4.



So two pendulums * connected by a spring represent an exact analogy with electrically-coupled circuits. Moreover, they may be used to elucidate the case of inductive coupling with the same success as the models of Prof. Barton and Mr. Jackson, because the coupling in their models is also performed by means of displacement itself and not by means of its second differentiation. The simplicity of theory † and some little preferences of easiness and commodity of experimentation, make the described model suitable for laboratory work ‡, as well as for demonstration use.

The above theory is illustrated here with a few curves only, because photographing is very dear in Russia. The curves Nos. 1–4 (Plate XIX.) are obtained with the pendulums of unequal lengths ($l_1 : l_2$ about 1 : 2), Nos. 5–8 (Plate XX.) with equal lengths; Nos. 2–4 illustrate the formula (8) and

* Or two springs, in which case k_1 and k_2, their extension coefficients, must be put into the equations (1) instead of $\frac{m_1 g}{l_1}$ and $\frac{m_2 g}{l_2}$, but then experimental adjustment is more difficult and the damping is larger.

† Look at the contrast between (1) of this work and (27) and (28) of the first and (9) and (10) of the third papers of Prof. Barton.

‡ In this case students' familiarity at least with the elements of theory seems to be necessary.

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may be regarded as a mechanical analogy of Tesla's transformer; Nos. 7 and 8 relate to (9), in which case the pendulums are not interchangeable and show the effect of different initial conditions; Nos. 5 and 6 are obtained with equal masses and lengths, which is a special case of (8) and (10) simultaneously; No. 1 shows the general case (periods, lengths, and masses unequal). The couplings used are always given as percentages. The upper curves in all photographs with unequal masses relate to the heavier bob. The initial conditions are shown in most of the photographs by the sand traces which are plotted by the pendulums before starting. The damping was very small in these experiments and has therefore been neglected in the above theory. The case when it is large is reserved for a later paper.

In conclusion, I wish to express my sincere thanks to Prof. S. A Artzibysheff for giving me the idea of this work and kindness in putting at my disposal the instruments of the laboratory, and Prof. J. P. Krawetz, to whom I am indebted for many valuable suggestions.

Physical Laboratory of University,
Irkutsk, Siberia.
July 20, 1924.

LXIII. *A New Vacuum Thermoelement.*

By Dr. W. J. H. Moll *and* Dr. H. C. Burger *.

IN the application of the thermoelement for measuring radiation, the advantage of enclosing the element in vacuo has often been enunciated, and determinations have frequently been made of how much the sensitivity is increased by removing the air. The gain in sensitivity varies considerably, according to differences in the form of the element and the properties of the metals used, but is often rather important (5 to 10 fold).

The sensitivity of a thermoelement of given components is determined by the temperature difference of both junctions for a given radiation striking one of them. If none of the energy received were lost, the temperature of the exposed junction would rise without limit; in reality an equilibrium will be reached in which the energy received is equal to that lost. In the case of thermoelements in air, the energy is led off: (1) by the air, (2) by conduction through the metals, (3) by radiation. A great gain of sensitivity caused by exhausting means only that loss through the air was predominant previously.

* Communicated by Prof. O. W. Richardson, M.A., D.Sc., F.R.S.

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The sensitivity of a vacuum-element of given components depends wholly on the heat conduction through the metals. The energy lost by conduction must be minimal, or better must be small as compared with the unavoidable loss by radiation. When this is the case, the effect of exhausting may become enormous. In our vacuum-elements the sensitivity is about 300 times as great as in air. A decrease of the leading away of the heat by conduction, however, implies an increase of the electrical resistance, and therefore should not be exaggerated. There will exist a *conditio optima*, i. e., the resistance of the thermoelement must be adapted to that of the galvanometer which is used to indicate the thermoelectric current. Anyhow there will exist for given components an ideal sensitivity of the thermoelement, an impassable limit, where the only loss of energy is through radiation.

This ideal sensitivity, viz. the case of equilibrium of radiation, may be computed easily for a given combination of metals.

Let d be the thickness of the receiver, O its area, r_1 and r_2 the mean reflecting power of front and back surfaces, c the specific heat and ρ the density of the material from which the receiver is made, I the radiation (in cal. per cm.^{2} and per sec.), T the absolute temperature of the receiver, and σ the constant of radiation $= 1{\cdot}38 \times 10^{-12}$ cal./cm.^{2} sec.

Then the constant of external thermal conduction h is

$$h = (1 - r_1 + 1 - r_2) \,.\, 4\sigma T^3.$$

The energy received per sec. $= I \,.\, O \,.\, (1 - r_1)$.

The energy lost per sec. $= h \,.\, O \,.\, \Delta T$,

if ΔT is the temperature difference between the element and the surroundings. This difference is a consequence of the radiation received.

The condition of equilibrium is

$$I \,.\, O \,.\, (1 - r_1) = h \,.\, O \,.\, \Delta T,$$

or

$$\Delta T = \frac{I\,(1 - r_1)}{h}.$$

In order to derive the sensitivity, let p be the thermoelectric power of the combination in volts, then the electromotive force E of the thermoelement is

$$E = \frac{I \,.\, (1 - r_1) \,.\, p}{h},$$

and its ideal sensitivity $S = \frac{E}{I} = \frac{1 - r_1}{h} p$.

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For a given thermocouple the ideal sensitivity may thus be computed, and one can compare this figure with the real sensitivity found by experiment. In this way one has a good knowledge of how far the loss of energy by conduction (and eventually through the air) is negligible.

As a matter of course it is also possible to compute the decrease of sensitivity caused in a vacuum-element by conduction, when the dimensions and the heat conductivity of both metals are known. From such computations we got the conviction that it must be possible to approximate to the ideal sensitivity rather closely.

The ordinary method of constructing thermoelements implies a fairly good heat conduction. The best elements consist of a silver wire and a quite thin rod of bismuth, soldered together with an alloy of low melting-point. Silver has a high conductivity, the bismuth part has a cross-section which is relatively quite large. As the length of these elements was limited by practical reasons, the loss of energy by conduction was by no means negligible.

The usual method of construction involves moreover another and more serious disadvantage. The quickness of response of such elements even in contact with the air is rather poor. When now the air is expelled, and accordingly the sensitivity increased, the slowness of the apparatus becomes uncanny. The great heat-capacity of the element and especially of the solder is responsible for this.

As we proceeded with the construction of our vacuum-thermoelement, we were convinced that the direction in which we had to improve the element was to reduce the thickness of the metals, the solder, and the receiver to a minimum This measure would have the advantage of decreasing the heat-conduction and thus increase the sensitivity, and at the same time would improve the quickness.

As to the quickness attainable, it could be estimated beforehand. The computation of the quickness of a thermoelement becomes somewhat uncertain if the loss of energy by conduction plays a predominant part, since in that case the notion of quickness is indefinite. It is possible, for instance, that with a thermoelement 50 per cent. of the final electromotive force is reached quite rapidly, while it takes a very long time before 99 per cent. of this final value is attained. But since we expected to obtain almost the condition of equilibrium of radiation, a computation on the premise of a heat-conduction zero would mean a fair approximation.

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For that case (no other loss of energy than by radiation), the quickness of the thermoelement may be derived from a simple calculation. Using the same symbols as above, we will consider a thermoelement, exposed to radiation for some time, the radiation being intercepted at a given time $t=0$, and calculate the rate at which the temperature-difference between the element and the surroundings falls off. The temperature-difference existing at a time t will be expressed by

$$\Delta T \,.\, e^{-\frac{t}{t_0}},$$

where

$$t_0 = \frac{d \,.\, \rho \,.\, c}{(1-r_1+1-r_2) \,.\, 4\sigma T^3}.$$

Now the "quickness" of the thermoelement may be defined as the time θ elapsing before ΔT has attained 1 per cent. of its initial value. As $e^{-\frac{\theta}{t_0}}=0{\cdot}01$ means $\theta=4{\cdot}38\ t_0$,

$$\theta = 4{\cdot}38 \frac{d \,.\, \rho \,.\, c}{(1-r_1+1-r_2) \,.\, 4\sigma T^3}.$$

In order to give a numerical example, we will apply this formula to the new thermoelement described further on. Of one of these elements the constants were approximately

$$d=1{\cdot}1\times 10^{-4},\ \rho=8{\cdot}5,\ c=0{\cdot}097,\ r_1=0{\cdot}10,\ r_2=0{\cdot}70,\ T=300.$$

The computed "quickness" θ is 2·3 sec., a value which is in fair agreement with that given by experiment.

Before we proceed to a detailed description of the new thermoelement, we will lay stress upon what in our eyes is a great advantage of the vacuum. The presence of air may give rise to unexpected and annoying perturbances. As a matter of fact, slight adiabatic variations of the air pressure change the temperature of a junction, especially if its heat-capacity is small. Besides one has ever to be apprehensive of convection of the air surrounding the element, brought about by outside circumstances. By a sufficiently high vacuum these errors are avoided, and the reliability of the instrument is greatly increased.

In order to minimize the heat conduction and at the same time the heat capacity of the thermoelement, we made use of the so-called thermofoil, described elsewhere *. This material is constructed in the following way. Two rather thick plates (*e.g.* of manganin and constantan) are soldered

* Proc. of the London Phys. Soc. xxxv. p. 258 (1923).

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together with silver. The superfluous silver is polished away, after which a narrow seam of silver remains. The bimetallic plate is then rolled out in the direction of the seam. In this process the seam is practically not broadened, and it has been found possible to prepare in this way a quite thin foil, consisting of two sheets of metal connected by a silver seam, the silver having the same thickness as the metals. By simply cutting this thermofoil into narrow strips, a large number of thermoelements is obtained.

These elements are applied in the construction of the thermopiles which have been described by one of us. The thickness of the elements was about 0·005 mm. The quickness of these piles (an equilibrium is reached within 2 seconds) is to a great part due to the effective heat transport by means of the air between the strips and a heavy plate of copper.

If such a thermopile is evacuated, its sensitivity increases considerably, but at the same time it loses its quickness. We commenced our investigations with an element of 0·005 mm. thickness and 15 mm. long. It needed 12 seconds to come to equilibrium. As compared with other vacuum thermoelements this result was not bad *, but we aimed at a quickness of the same order as was attained with the thermopiles mentioned above.

We now tried to refine the process of rolling out, and with much care and a great loss of material we succeeded in preparing small pieces of thermofoil with a thickness of only 0·001 mm.

Fig. 1.

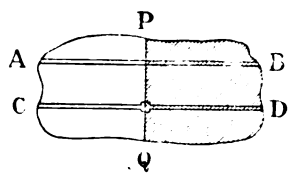

Fig. 1 represents a piece of thermofoil on an enlarged scale. P Q is the narrow seam of solder. A strip A B cut

* There exists in the literature a communication about a vacuum thermoelement with a formidable quickness. Pettit and Nicholson (Astroph. Journ. lvi. p. 295 (1922)) prove by calculation that their element has a quickness of 0·006 sec.! They made a mistake in their reasoning. An experiment would have shown that the quickness of this element is of the order of 30 sec.

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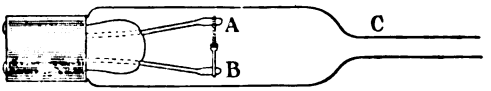
from this foil forms a linear element *. For some applications it was desirable to have a receiving area of greater extension, and for that purpose we constructed elements of the form C D. It will be clear that cutting such elements would be practically impossible. We succeeded by covering the whole back surface of the foil and on the front only the part C D with a varnish, and dissolving the surrounding foil in nitric acid.

One side of the sensitive part of the thermoelement had to be blackened. Soot was inappropriate for this purpose, as its heat conduction *in vacuo* is too small. We applied an aqueous solution of colloidal carbon, spread out in a layer of about 0·001 mm. thickness.

An element of one or the other form is now mounted within a glass tube, in the same manner as is usual in the construction of electric lamps. The two electrodes are heavy wires, and the element is soldered at A and B (see fig. 2). The narrow part of the tube is connected to a

Fig. 2.



high-vacuum pump, and the evacuated thermoelement is heated during an hour to 300° C. in order to expel all gas residues from the glass and the metal parts. Mercury vapour and other impurities are frozen out with liquid air, and finally the tube is melted off at C.

The heating during the evacuation is necessary as without this precaution the vacuum is not durable. With the older types of thermoelements this heating was impossible, since the solder used had too low a melting-point. The thermofoil, however, is soldered with silver and sustains a heating to 400°.

The sensitivity, the quickness, etc. of these thermoelements differs somewhat for the various specimens. But we will mention some average data, in order to give an impression of the features of the instrument.

The sensitivity of the element with an extended junction (of form C D, see fig. 1) is from 50 to 70 per cent. of the ideal. The linear elements have a relatively greater heat

* Such an element of 0·05 mm. breadth and 8 mm. length has a resistance of 15 ohms, and weighs only 0·003 milligram.

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conduction, though even in this case the loss through conduction is not much greater than that through radiation. An element of form C D, with a receiving area of 1 mm.^{2}, required $\frac{1}{15} . 10^{-6}$ cal. sec.$^{-1}$ for giving 1 microvolt. A linear element of 0·05 breadth, when receiving radiation from the same source as the former one, and along the same length of 1 mm., gives only $\frac{1}{3}$ microvolt. But as compared with the former thermoelement, the receiving area of the linear one is only $\frac{1}{20}$ mm.^{2} Accordingly it needs only $\frac{1}{20} \cdot \frac{1}{15} \cdot 10^{-6}$ cal. sec.$^{-1}$ to give $\frac{1}{3}$ microvolt, *i.e.* 10^{-8} cal. sec.$^{-1}$ per microvolt.

The mean error of the galvanometer we used was $\frac{1}{1000}$ microvolt, corresponding to less than $\frac{1}{2000}$ erg per sec.

The quickness of response is quite satisfactory. When radiation is admitted, the element reaches its final temperature within two or three seconds.

The resistance of these thermoelements is about 10 to 20 ohms.

Physical Laboratory
of the University.
Utrecht, June 1925.

LXIV. *The Thermo-Relay.* *By* Dr. W. J. H. Moll *and* Dr. H. C. Burger *.

To measure a small angle through which a body rotates, use is very frequently made of a little mirror fixed to the body, the mirror reflecting a beam of light, and projecting a spot (provided with an index) on to a scale. The great advantage of this method lies in the possibility of using a large scale distance, and therefore getting great displacements of the spot for relatively small rotations. But it is of no use to exaggerate this distance. Enlarging the scale distance above a certain limit yields for a given rotation a greater displacement it is true, but the sharpness of the index is worse, and the accuracy obtained remains practically the same. It is for the same reason that a scale is never subdivided in tenths of a mm. and the spot read off with a magnifying glass; if magnified, the image loses its sharpness and no gain in accuracy would have been reached. As a matter of fact, in all measurements of this sort the accuracy attainable is limited by the defective sharpness of the light-index.

* Communicated by Prof. O. W. Richardson, M.A., D.Sc., F.R.S.

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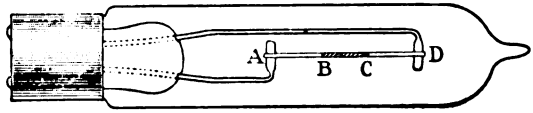
In the following lines we will describe a simple method of measuring rotations so small as to be unmeasurable in the usual way. This method makes use of the above-mentioned reflecting mirror, but its accuracy is absolutely independent of the sharpness of the spot. It may even be applied in connexion with a mirror of quite bad quality. Moreover, it permits a photographic registration

The principle of the new method is the generating of a thermo-electric current by means of the spot of light. This current is indicated by a galvanometer, and the deflexions may either be read off or recorded photographically on a registering drum.

The new apparatus (the thermo-relay) is constructed in the following way. From a piece of "thermofoil" *) a strip ABCD (fig. 1.) is cut out. The parts AB and CD are of

Fig. 1.



constantan, the part BC of manganin. This strip is blackened and mounted in an evacuated glass vessel, in the same manner as is usual in the construction of electric lamps. The thermo-relay is enclosed in a double brass tube provided with slits in front of the strip.

When now a spot (sharp or unsharp) is projected upon the middle part of the strip, both junctions will be heated, and a galvanometer connected to the relay will show a deflexion. By shifting the relay in the direction of the strip, this deflexion can be made zero, both junctions having then the same temperature. A small rotation of the mirror which gives a displacement of the spot, *e. g.* to the right, will raise the temperature of the right junction above that of the left, and will cause a galvanometer deflexion. A rotation of the mirror in the other direction will give an opposite deflexion. If the displacements of the spot are not too great, the galvanometer deflexion is proportional to the rotation.

It is a matter of course that the source of light must have an invariable intensity. An incandescent lamp with short spiral connected to some accumulators will do perfectly well. If the mirror is small, it is advisable to use the

* *Suprà*, p. 618.

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following arrangement. The spiral of the lamp is projected by a lens on to the little mirror; a second lens, placed in front of the mirror, converges the reflected beam of light, and a cylindrical lens, placed in front of the slit of the brass tube, makes an elongated image of the mirror on the strip. The thermo-currents generated by an arrangement of this sort will be strong enough for most applications. With an incandescent lamp of 16 candles, a mirror of only 5 mm. diameter, and a good coil-galvanometer, a rotation of the mirror through an angle of $\frac{1}{10}$ sec. gives a measurable galvanometer deflexion.

This very high sensitivity of the thermo-relay is due to the fact that there is no loss of energy through the air, and that the loss by conduction along the very thin strips (thickness about 0·001 mm.) is quite small. The vacuum excludes, moreover, all disturbances which would arise if the strip were surrounded by air, and consequently the thermo-relay is practically free from perturbations. If necessary, it can be used in connexion with a very sensitive galvanometer.

A second advantage of the extreme thinness of the strip is the quickness in response of the thermo-relay. In combination with a quick and aperiodic galvanometer, a deflexion reaches its final value within three seconds.

One of the applications of the thermo-relay will be described in the following paper, viz. the amplification of the sensitivity of a galvanometer. It will be shown there that a tenfold or a hundredfold amplification can easily be reached by throwing the spot reflected by the galvanometer mirror on a thermo-relay, and connecting the relay to a second galvanometer.

Physical Laboratory
of the University.
Utrecht, June 1925.

LXV. *The Sensitivity of a Galvanometer and its Amplification.* *By* Dr. W. J. H. Moll *and* Dr H. C. Burger *.

An important property of the galvanometer is its sensitivity. For most applications it is the volt-sensitivity that matters—that is to say, the deflexion on a scale at one metre for one microvolt. The importance of this figure, however, is generally over-estimated. In all publications about investigations where the highest achievements of the galvanometer are wanted, this figure is

* Communicated by Prof. O. W. Richardson M.A., D.Sc., F.R.S.

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mentioned as its most salient feature ; in the construction of a new galvanometer the main object is usually to attain an extreme sensitivity.

Yet it will be evident that the essential feature of a galvanometer intended for the study of the weakest effects is not the bigness of the deflexion for one microvolt, but the smallness of the electromotive force which can be read off with certainty. It is true that the latter specification is not independent of the conditions under which the galvanometer is used, and that therefore it is necessary to detail these conditions; a reference, on the other hand, to the mere sensitivity has for practical purposes no value at all. In all galvanometer work one has to struggle with disturbances. A galvanometer with a high sensitivity, but strongly subject to perturbations, will be of little use for the measurement of small electromotive forces.

The disturbances which limit in practice the efficiency of a galvanometer may be divided into two kinds : disturbances peculiar to the galvanometer as such, and those acting in the outer circuit. The first are dependent in a high degree on the place where the apparatus has been installed ; but under the same circumstances of location various galvanometers are affected by perturbations to a quite different degree, and thus the necessity presents itself of characterizing the quality of the galvanometer in this respect. For this purpose one could proceed in the following way. The galvanometer in question is installed in a cellar-vault, placed on a wall-bracket or suspended, and short-circuited. During the night one observes the zero, and an estimation is made of the mean deviation. When the sensitivity of the galvanometer is known, one can derive from these observations the mean error, expressed in microvolts, of the galvanometer under most favourable conditions. This mean error has to be considered as the most valuable information about the galvanometer.

As compared with the disturbances met with by the galvanometer itself, those originating in the outer circuit are usually predominant. In so far as they have a regular course, they may be taken into account ; a skilled experimenter can take account as well of suddenly arising perturbations. There remains, however, a mean error resulting from the outer disturbances, which frequently is much greater than that peculiar to the short-circuited galvanometer.

Now the amount of this mean error is *ceteris paribus* not the same for different galvanometers. In this respect the

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quickness of the galvanometer plays an important part which is usually under-estimated. While a very slow apparatus integrates the various disturbing effects, it often becomes possible with a quick one to discover disturbances of short period. Once recognized as such, they may be taken into account.

There is still another reason why with a quick galvanometer the mean error caused by disturbances in the outer circuit may be made smaller than would be possible with a slow one. With a sufficiently quick apparatus it is possible to distinguish the different disturbances from each other. The closing of a door, the passing in the street of a carriage, currents caused by induction by a faulty insulation or a bad contact, thermo-currents, etc.—all give their characteristic fluctuations of the spot. The differences in their aspect appear in a striking manner when the fluctuations of the spot of a quick galvanometer are registered. Not infrequently one succeeds in tracing in this manner the presence of known and unknown disturbances, and can then exclude them.

We think, therefore, that the efficiency of a galvanometer for the study of weak effects should not be judged by its sensitivity. The mean error, expressed in microvolts, of the galvanometer when short-circuited and installed under the most favourable conditions is one criterion, and the galvanometer's quickness is the second.

It is possible to amplify the sensitivity of a galvanometer by means of a "thermo-relay *".

A beam of light, emerging from a little incandescent lamp, is reflected by the mirror of the galvanometer and thrown on a thermo-element of special construction; it generates a thermo-current, which is indicated by an auxiliary galvanometer. The size of amplification depends on the intensity of the spot projected on the thermo-relay, and can be adjusted at will by regulating the lamp's current. Even with a galvanometer-mirror of small dimensions (*e.g.* 5 mm. diameter) it is easy to attain a hundred-fold amplification.

When this method is applied to one of the usual very sensitive galvanometers, an enormous sensitivity may be reached. The proceeding, however, as a rule has no meaning, because the errors are magnified to the same amount, and the mean error expressed in microvolts usually

* *Suprà*, p. 624.

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remains the same. The method will give only a real advance if used in combination with a galvanometer the zero of which is so steady that the irregular fluctuations of the spot are smaller than the least readable deflexions.

We investigated the efficiency of this method of amplification with a coil-galvanometer of special construction, designed by one of us *. Its great zero-steadiness is principally due to the fact that the coil is not suspended as is usual, but stretched between two wires. When used in the ordinary way, and giving a spot on a scale at one metre, readings can be made with a precision of $\frac{1}{10}$ or $\frac{1}{20}$ mm. Its steadiness would permit a reading to $\frac{1}{100}$ mm. and less; but even with the best mirror the precision of the reading is limited by the defective sharpness of the light-index. This galvanometer has a time of indication of less than two seconds; its resistance is about 50 ohms.

We installed the apparatus on a wall-bracket in a room on the second floor of our Institute, which is situated within the town and a short distance from the traffic. The outer circuit was formed by a resistance-box, by means of which small electromotive forces could be inserted.

Fig. 1 *a* gives a reproduction on a true scale of a photographical registration of the zero during eight minutes. Two minutes after beginning, an electromotive force of ten microvolts was inserted during ten seconds, and four minutes after that an electromotive force of one microvolt. The reading is certain to about $\frac{1}{20}$ mm., corresponding to a mean error of 25×10^{-9} volt.

Fig. 1 *b* gives the line when a 5-fold amplification had been applied. This curve has been recorded therefore by an auxiliary galvanometer, the latter being of the same type as the primary one. As is obvious from the picture, the quickness of response has become somewhat smaller, but the reading is still certain to $\frac{1}{20}$ mm. The mean error has been reduced to about 5×10^{-9} volt.

Fig. 1 *c* shows a 25-fold amplification of the sensitivity. The zero-line is no longer smooth; the error of reading has become greater, and amounts to about $\frac{1}{10}$ mm., corresponding to 2×10^{-9} volt.

When the sensitivity is still more amplified, the real progress is but small, as fig. 1 *d*, a 100-fold amplification, shows. The mean error is here about 1×10^{-9} volt. Further amplification of the sensitivity would be of no use.

The conspicuous disturbance, visible in this figure (fig. 1 *d*),

* Proc. Phys. Soc. xxxv. p. 253 (1923).

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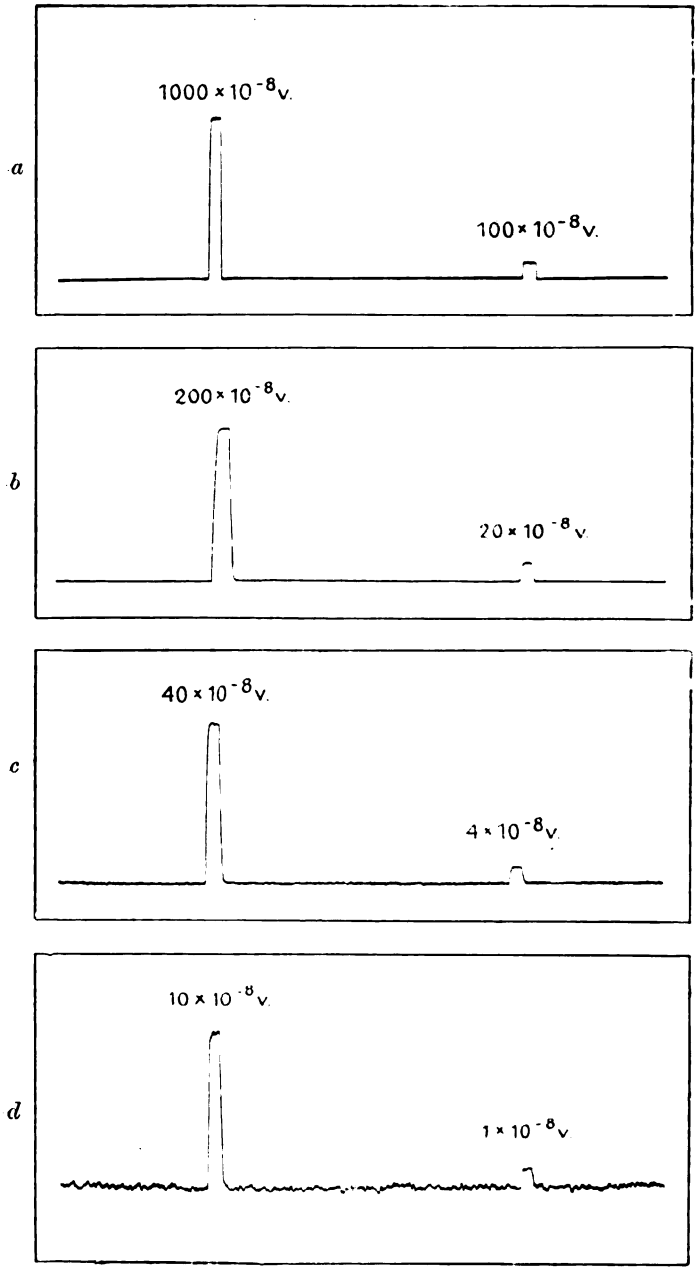
Fig. 1.



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has been caused in all probability by microseismic perturbations. It has a period of about six seconds, and has the same character at daytime as in the night. That a slow motion to and fro of the walls entails rotations of the mirror must be a consequence of a slight asymmetry of the coil. We are hopeful to succeed in reducing this asymmetry, and to raise by that means the efficiency of our galvanometer still considerably.

That it has been possible to attain such a high sensitivity, and to overcome all other disturbances, is principally due to the quickness of our combination. Indeed, various perturbations became manifest as we gradually increased the sensitivity, but by recording the zero photographically they could be identified and eliminated one after the other.

Physical Laboratory
of the University.
Utrecht, June 1925.

LXVI. *The Piezo-Electric Oscillograph* *.
By A. B. Wood, *D.Sc., F.Inst.P.* †

[Plates XXI. & XXII.]

In the February issue of the Philosophical Magazine an account is given by C. E. Wynn-Williams, M.Sc. (pp. 289–313) of a piezo-electric oscillograph. Mention is made of more or less unsuccessful attempts to utilize quartz strips for the purpose in view, but these have been abandoned as being too insensitive. Rochelle salt, on the other hand, is considerably more sensitive, but possesses certain disagreeable features mentioned in the paper. The paper concludes by a statement: "If sufficient magnification could be obtained a quartz oscillograph would probably, owing to the very definite physical properties of this substance, be superior to one of rochelle salt."

It is the object of this note now to point out that the quartz oscillograph is by no means so impracticable as might be supposed. In 1920 the author designed and tested two types of quartz strip oscillograph which gave very satisfactory results. A description of these instruments is given in Patent No. 180,787, March 1921, but it may not

* The oscillographs described were designed and constructed in 1920, and the paper is now published by permission of the Admiralty.

† Communicated by Mr. F. E. Smith, C.B.E., F.R.S.

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be out of place to make further reference to them here. The two types will be described as the single-strip and the double-strip oscillographs *.

I. *Single-Strip Oscillograph.*

In principle, this is essentially the same as that described by Mr. Wynn-Williams (and illustrated in his paper in fig. 4, p. 296), but differs in important details. The strip of quartz is cut with its thickness 'e' in the direction of the electric axis, its length 'l' in the third direction, and its breadth 'b' in the direction of the optic axis. When a p.d. of V electrostatic units is applied across the electric axis then the dilatation δ in the direction of its length is given by

$$\delta = K\frac{l}{e}V,$$

where K is a constant depending on the piezo-electric properties of the crystal.

In the case of quartz $K = 6{\cdot}45 \times 10^{-8}$.

It will be seen that the change of length of the crystal is directly proportional to the applied voltage, and to the ratio of length to thickness. See Table I. In Mr. Williams's experiments a slab of crystal 5 cm. long and 0·3 cm. thick was employed, whence

$$\delta = 1{\cdot}07 \times 10^{-6}\,V \text{ cm.},$$

or if V is expressed in volts,

$$\delta = 3{\cdot}5 \times 10^{-9}\,V \text{ cm.};$$

i. e., for $V = 1000$ volts

$$\delta = 3{\cdot}5 \times 10^{-6} \text{ cm.}$$

This is a very small deflexion, but it is possible to increase it considerably. In the first place, by reducing the thickness of the slab from ·3 cm. to ·03 cm. the value of δ is multiplied 10 times. By means of a simple optical lever device, shown in fig. 1 *a*, the resulting dilatation of the slab may again be magnified 10^4 times. In the arrangement shown, an oscillograph mirror (about ·5 × 1 mm.) is pivot d on parallel knife-edges spaced about 0·1 mm. apart, and a spot of light reflected from it on a scale or on a photographic film at say 1 metre distance. One of the knife-edges is attached to the top of the slab, whilst the other is fixed firmly to the

* The properties of single and double piezo-electric strips, as utilized in the design of these Oscillographs, are described in 'Œuvres de Pierre Curie,' Paris (Gauthier Villars, 1908), pp. 35–55.

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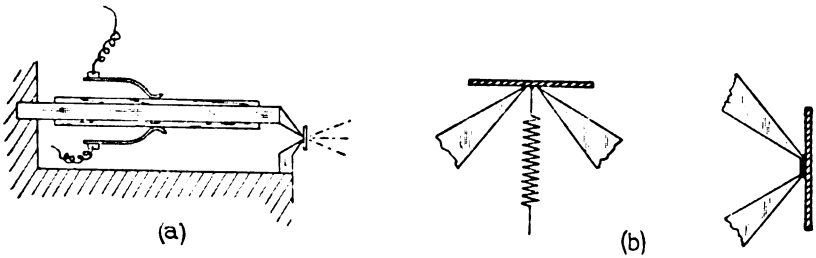
base of the oscillograph. The magnification factor of this arrangement is therefore $2 \times 100/\cdot 01 = 2 \times 10^4$. Thus the deflexion '$d$' per 1000 volts will be $2 \times 10^4\delta$, which becomes 0·43 cm. for a crystal slab of thickness 0·5 mm. An oscillograph constructed on this principle gave results in accordance with the theory. The mirror was held on the knife-edges by an elastic cement (see fig. 1 *b*) (a spring would probably serve the same purpose).

Fig. 1.



Single-Strip Type.

It is to be noted that in this arrangement the inertia of the moving parts is very small, but it should be observed also that the force holding the mirror on the knife-edges must be considerable in order that the acceleration of the vibrating strip of quartz should never exceed that due to the restoring action of the spring. The natural frequency of this type of oscillograph is high, corresponding to the longitudinal vibration of the strip (if 'l' = 5 cm. frequency 25,000 app.). The insulation is of course exceptionally good, and both positive and negative deflexions are strictly proportional to voltage. In these respects quartz is superior to rochelle salt.

II. *Double-Strip Oscillograph.*

The sensitivity of the single-strip quartz oscillograph referred to above is inversely proportional to the thickness of the strip and directly proportional to the length. Limits are set to the former by the mechanical and electrical strength of the crystal, whilst the length is limited by the maximum size of crystals obtainable. By employing a device, well known in the study of thermal expansion, it is possible to increase still further the sensitivity of the quartz strip oscillograph. This is accomplished as follows. If two strips of crystal (of the nature just described) are cemented

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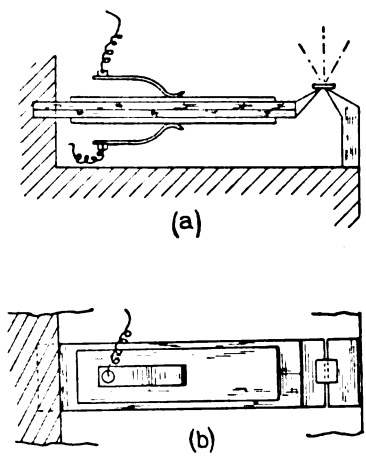
together in opposite senses—so that one layer expands whilst the other contracts—the bi-plate assumes a curvature whose radius depends on the amount of dilatation. If 'l' and 'e' represent the length and thickness of each of the layers and V electrostatic units the p.d. applied to the outer faces, then the lateral displacement of the unclamped extremity of the compound strip will be

$$\delta = \tfrac{3}{4} K \cdot \frac{l^2}{e^2} \cdot V,$$

the method of mounting being illustrated in fig. 2 (sectional

Fig. 2.



Double-Strip Type.

elevation in a, plan in b). The dilatation is now proportional to the square of the ratio l/e—indicating a greatly increased sensitivity.

If quartz is used, $K = 6{\cdot}45 \times 10^{-8}$. Taking $l = 5$ cm. and $e = 0{\cdot}05$ cm.,

$$\delta = 1{\cdot}6 \times 10^{-6}\ V \text{ cm. if V is expressed in volts.}$$

With an optical magnification of 2×10^4 the deflexion 'd' at 1 metre will be ·032 V cm., *i. e.* 0·32 mm. per volt.

It will at once be seen that this represents a very considerable increase in sensitivity over the single-strip type of oscillograph, in the example given the increase being in the ratio $\frac{3}{4}\, l/e$, i. e. 75 times. (See Table II.)

The natural frequency of this type is of necessity rather

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low *, for now we are dealing with the transverse vibrations of the piezo-electric strip. The pronounced resonance is very apparent when an A.C. voltage of continuously variable frequency is applied. The band of light produced by the mirror oscillations widens out rapidly near resonance, and the strip itself emits a loud note corresponding to the applied frequency. This resonance can be reduced in several ways, one of the most simple depending on the choice of the medium for mounting the mirror on the knife-edges. Photographs of two early patterns of quartz oscillograph are shown in Pl. XXI. fig. 3—Single Strip (*a*), Double Strip (*b*).

With either type of oscillograph the dimensions of the crystal slab employed are determined by the voltage-range for which the instrument is to be used. The thinner the slab, the lower will be the voltage-range that it will detect.

The fact that crystals of rochelle salt show much greater piezo-electric effects than quartz was realized from the first, but owing to the somewhat irregular behaviour of rochelle salt as regards sensitiveness and insulation and its liability to breakdown under electric stress, it was considered desirable to develop the quartz type for metrical purposes.

The following tables are inserted as a convenient means of comparing the sensitivities of the single- and double-strip oscillographs, and to provide a basis of comparison with observations of the behaviour of the two oscillographs illustrated in fig. 3 *a* and *b* (Pl. XXI.).

TABLE I.

The table indicates the increase of sensitivity with the ratio length/thickness in the case of the *single-strip quartz oscillograph*.

Optical magnification assumed $= 10^4$.

Length $l = 5$ cm.

K for quartz $= 6{\cdot}45 \times 10^{-8}$.

Thickness 'e' cm.	l/e	Sensitivity (at 1 metre).	
		cm. per volt.	Volts per cm.
0·5	10	$2{\cdot}15 \times 10^{-5}$	46500
·2	25	$5{\cdot}4 \times 10^{-5}$	18500
·1	50	$1{\cdot}07 \times 10^{-4}$	9350
·05	100	$2{\cdot}15 \times 10^{-4}$	4650
·02	250	$5{\cdot}4 \times 10^{-4}$	1850
·01	500	$1{\cdot}07 \times 10^{-3}$	935

* *E. g.* 1350 ~/sec. in one oscillograph.

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The single-strip oscillograph shown in fig. 3 *a* has a length of 5·1 cm., thickness ·06 cm., i.e. $l/e = 85$. The deflexions obtained by the application of positive and negative potentials up to ± 6000 volts indicated a linear relation and a sensitivity of approximately 6000 volts per cm., which is in moderately good agreement with the tabulated values in Table I. The natural frequency of the oscillograph was not determined experimentally, but calculation indicates a value of the order of 20,000 ~/sec.

In fig. 3 *c* is shown a single-strip rochelle salt oscillograph, the strip having a length of 5·2 cm., thickness 0·47 cm., whence $l/e = 10{\cdot}6$. The D.C. sensitivity is approximately 10 volts per cm. at a metre, corresponding to about 4000 times the equivalent sensitivity of a quartz strip of the same dimensions. The natural frequency of the rochelle salt strip shown is between 3000 and 4000 ~/sec.

Table II.

The table indicates the increase of sensitivity with the ratio length/thickness in the *double-strip or bi-plate quartz oscillograph.*

Optical magnification assumed $= 10^4$.

Length $l = 5$ cm.

K for quartz $= 6{\cdot}45 \times 10^{-8}$.

Thickness 'e' cm.	l/e.	l^2/e^2.	Sensitivity.	
			cm. per volt.	Volts per cm.
0·5	10	100	0·00016	6250
·2	25	625	·001	1000
·1	50	2500	·004	250
·05	100	10000	·016	62
·02	250	62500	·10	10
·01	500	250000	·4	2·5

The double-strip oscillograph shown in fig. 3 *b* consists of two quartz plates each of length 5 cm., thickness ·08 cm., *i.e.* the length/thickness ratio $= 62{\cdot}5$.

As in the case of the single-strip type, the deflexions varied linearly with voltage, positive or negative, and a sensitivity of 170 volts per cm. at one metre was observed—in good agreement with values given in Table II. The natural frequency of this oscillograph was 1350 ~/sec. approximately. When opportunity offers, it is proposed to

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construct a double-strip rochelle-salt oscillograph. It is to be anticipated that this would be extremely sensitive even at high natural frequency.

A number of A.C. records obtained with the piezo-electric oscillographs are shown in fig. 4 (Pl. XXII.). (A dropping-plate camera was used.)

The excellent paper of Mr. Wynn-Williams and the oscillograph records obtained by him using rochelle salt serve without further remarks here to emphasize the advantages of the piezo-electric oscillograph. Of course there are certain obvious limitations as compared with other forms of electrostatic oscillograph, the sensitivity, for example, being considerably less than that of the E.S. string oscillograph. On the other hand, its simplicity and cheapness of production are points in its favour.

LXVII. *A Mathematical Statistical Investigation concerning Sub-electrons* *. *By* HERBERT DAECKE, *Dr. rer. nat. of Hamburg* †.

THE controversy concerning sub-electrons has by no means been definitely decided, either in favour of Ehrenhaft ‡ or of Millikan § in spite of the fact that this controversy has been of sixteen years' duration. The lack of agreement between Ehrenhaft and Millikan is indeed to-day partly removed by the fact that all physicists who have measured electrical charges of particles of a sufficiently small radius according to the method of Ehrenhaft have found charges that substantially fall short of the value $e=4{\cdot}77\times10^{-10}$ E.S.U. for the elementary quantum of electricity. The difference consists only in the fact that whereas the one group regards the sub-electrons as actual, the other believes that the shortage in value is only an apparent one produced by various causes. So many different things are indeed cited as causes, that it seems entirely out of the question to take up a clear and unique position on the matter. One physicist refuses to accept as an explanation the causes

* Cf. *Phys. Zeitschr.* xxv. pp. 624–631 (1924), and the detailed treatment in *Zeitschr. f. Phys.* xxvi. pp. 552–575 (1925).

† Communicated by the Author.

‡ F. Ehrenhaft, *Anz. Wiener Akademie*, March 4, 1909; April 21, 1910; May 12, 1910; *Wiener Ber.* cxix. p. 815 (1910); *Phys. Zeitschr.* xi. p. 940 (1910); *Ann. d. Phys.* xliv. p. 657 (1914); lvi. p. 1 (1918); lxiii. p. 773 (1920).

§ R. A. Millikan, *Phys. Zeitschr.* xi. p. 1097 (1910); Phys. Rev. xxxii. p. 349 (1911); *Phys. Zeitschr.* xiv. p. 736 (1913); Phil. Mag. xxxiv. p. 1 (1917).

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cited by another, and indeed partly for good reasons. Some intimations are given in the following *.

O. W. Silvey †, working with Millikan, regards the particles which give charges smaller than e as impure mercury or as dust particles, and simply disregards them for subsequent computations. M. König ‡ and E. Radel §, following E. Regener ‖, put the responsibility for the shortage in value upon the gas which is supposed to surround the particle in the layer of 10^{-6}–10^{-5} cm. thickness. In a more recent paper of E. Wasser ¶, the proofs for this are made to appear unquestionably dubious. The hypothesis of Regener is likewise in other respects but weakly supported. This is shown not only by the decisive refutation on the part of a student of Ehrenhaft, Th. Sexl **, but also by the rejection of this assumption by R. Bär ††. Bär, however, also observed shortages. As K. Wolter ‡‡ had shown that these could not be explained by the invalidity of the Stokes-Cunningham law of resistance, Bär resorted for their explanation to the assumption of altered abnormally small densities. This assumption of Bär's has, however, met much the same fate as he himself imposed upon the hypothesis of Regener. F. Ehrenhaft §§ not only advances convincing opposing arguments, but L. Schiller ‖‖ likewise finds densities of 0·2 for platinium, for example, highly improbable. Schiller believes the shortages in charge to be explained by departures from spherical form.

One contradiction is here seen to follow upon another. A fitting treatment hence seems to me to be one which, unburdened by prejudice, examines the entire complex of facts not by purely physical, but by mathematical statistical methods.

The observations applied for our investigations are those of M. König ¶¶ on mercury in air and carbon dioxide gas, and those of E. Radel *** on mercury in air. On arranging

* In more detail in the articles cited in the first footnote on p. 637.

† O. W. Silvey, Phys. Rev. vii. pp. 87–105 (1916). *Cf.* also Y. Ishida, Phys. Rev. xxi. p. 561 (1923).

‡ M. König, *Zeitschr. für Phys.* xi. pp. 253–259 (1922).

§ E. Radel, *Zeitschr. für Phys.* iii. pp. 63–88 (1920).

‖ E. Regener, *Sitzungsber. d. Preuss. Akad.* (1920), pp. 632–641.

¶ E. Wasser, *Zeitschr. für Phys.* xxvii. pp. 226–236 (1924), in particular p. 231 *et seq.*

** Th. Sexl, *Zeitschr. für Phys.* xvi. p. 39 (1923).

†† R. Bär, *Ann. d. Phys.* lxvii. pp. 157–200 (1922).

‡‡ K. Wolter, *Zeitschr. für Phys.* vi. p. 339 (1921).

§§ F. Ehrenhaft, *Naturw.* x. p. 980 (1922).

‖‖ L. Schiller, *Zeitschr. für Phys.* xiv. pp. 6–13 (1923).

¶¶ M. König, *l. c.* *** E. Radel, *l. c.*

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their observations in order of decreasing radius, these observers record a point under which the charge is *substantially* less than $e = 4{\cdot}77 \times 10^{-10}$ E.S.U. (M. König gives the limiting radius $1{\cdot}2 \times 10^{-5}$ cm. for mercury in air, and 2×10^{-5} cm. for mercury in carbon dioxide gas; E. Radel the limiting radius 9×10^{-6} for mercury.) As my investigations are designed to make clear the relationships among the *sub*-electrons, I have applied this fact as a natural *basis of classification* for my statistics. The great significance of this step, which avoids using as statistical material those charges which lie close to $4{\cdot}77 \times 10^{-10}$ E.S.U. or multiples thereof, will be made clear on discussing the results obtained.

Of all the substances upon which observations of charge have been made with the Ehrenhaft condenser, mercury has been selected because a number of sources of error which are present for other substances disappear for mercury. Substantial shortages have not been established by all observers for oil and paraffin. Copper, sulphur, and selenium have firstly been comparatively little investigated, and secondly cannot lay the same claim to chemical definiteness and stability as can the noble metals *. Although it can hardly be expected that platinum, gold, and silver particles depart very strongly from spherical form, the sphericity of form of mercury particles is an indisputable fact †. Furthermore, mercury particles can, on account of their high coefficient of reflexion, be made visible in sizes in which particles of other substances (oil, glycerine, water) are completely imperceptible optically.

Let us now take from König's experiments those 24 values of the charge on mercury in air which substantially fall short of $e = 4{\cdot}77 \times 10^{-10}$ E.S.U. We may then propose the following question:—*How great is the probability that these* 24 *values are integral multiples of a fundamental charge* (e. g. of $0{\cdot}50 \,.\, 10^{-10}$ E.S.U.), *this fact being concealed only by the error dispersion*? This question is similar to the more previous one which inquires into the hypothetical fundamental charge of which the observed charges are integral multiples. It can be answered very well by means of a criterion for integers that R. v. Mises ‡ has set up by means of the cyclical theory of errors. He applied it at the time to atomic weights. If, namely, the 24 values of charge be plotted on a line which is then wound upon a circle of circumference 0·50, the criterion

* F. Ehrenhaft, *Sitzunzysbr. d. Wiener Akad.* cxxiii. [2*a*], p. 62 (1914).

† *Cf.* F. Ehrenhaft, *l. c.* pp. 87–95 and Table III.; also E. Wasser, *Zeitschr f. Phys.* xxvii. pp. 208–209, 211, figs. 1 & 2 (1924).

‡ R. v. Mises, *Phys. Zeitschr.* xix. pp. 490–500 (1918). Here is also given the exact meaning of the various quantities.

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for integral multiples is given by the magnitude

$$K = 2\pi C(kna)e^{kna\cos\alpha}$$

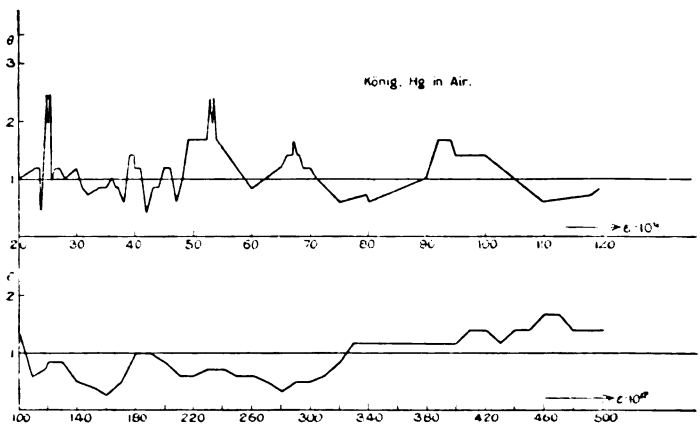
(n number of observations, a and α polar coordinates of the centre of mass of the statistical distribution, k coefficient of precision). The more K exceeds the value 1, the more plausible is the assumption that the values are integral multiples. If $K<1$, this assumption is to be repudiated. If K is exactly equal to 1, either assumption is equally justifiable.

For our problem concerning sub-electrons, we propose the following more far-reaching question: *For what value of* ϵ *does K attain a relative maximum?* To answer this question it would be necessary to compute K for many values of ϵ. As this would require an immense amount of work, we introduce a quantity Q which seems to give an excellent preliminary orientation concerning the maxima of K:

$$Q = \frac{Z_1 + Z_4}{Z_2 + Z_3}.$$

(Z_i number of observations in the ith quadrant after winding upon the circle.) Q is seen to be easily computable. At those points at which Q is a maximum K is to be more exactly computed.

Fig. 1.



We must finally say something concerning the justification of applying the cyclical theory of errors to a definite group of observations. This is demonstrated by the agreement of the theoretical error integral with the summation corresponding to the actual error distribution, this summation being representable as a step-like curve.

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Fig. 2.
König, Hg in Air.

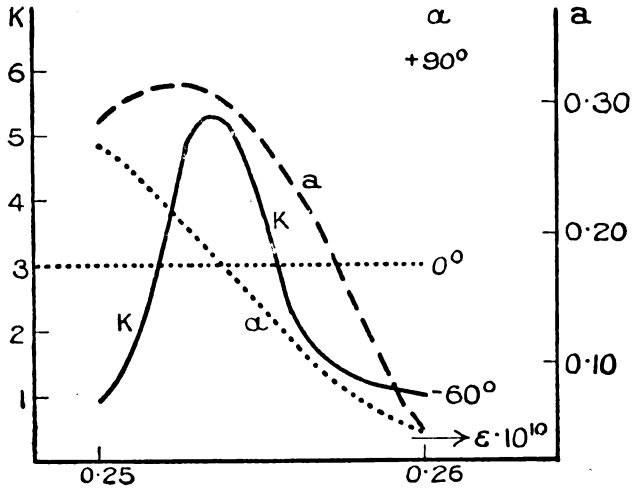
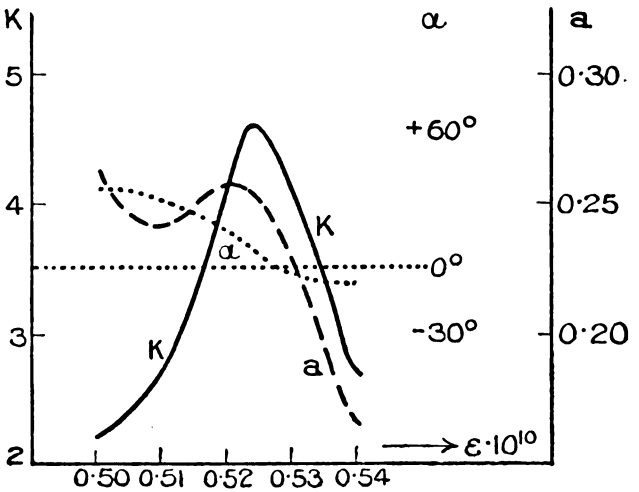


Fig. 3.
König, Hg in Air.



We give as an example the results for the observations of König on mercury in air. The Q-curve is shown in fig. 1. The maxima of Q are distinctly recognizable. The values of a, α, and K are more exactly computed for four points. (Figs. 2–5.)

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Fig. 4.

König, Hg in Air.

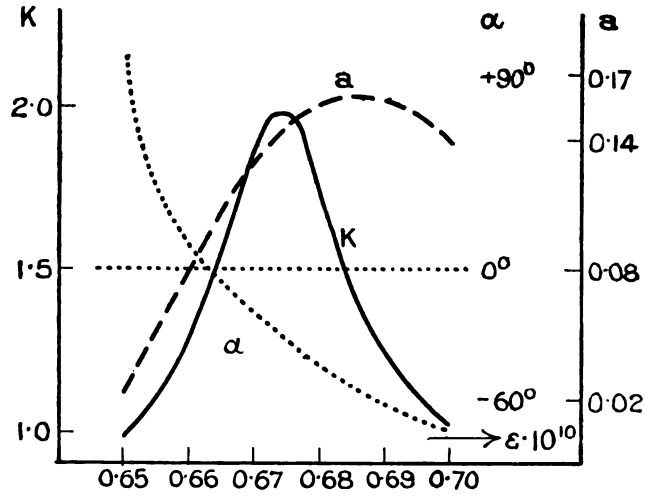
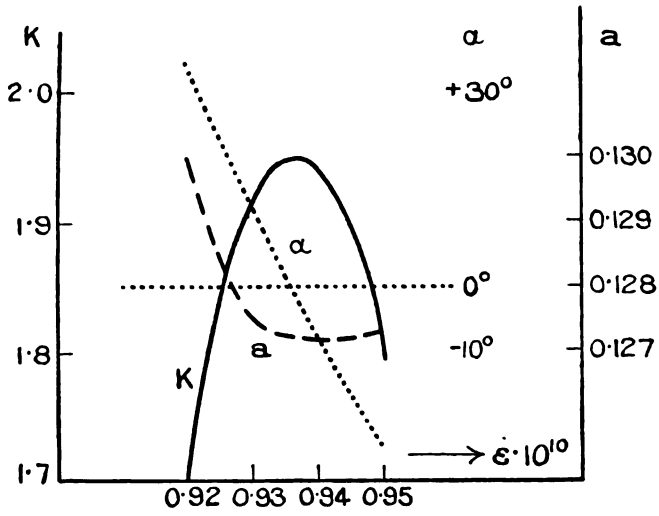


Fig. 5.

König, Hg in Air.



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One immediately notices the following remarkable fact :— *The four values of ϵ for which K is a maximum very nearly coincide with numbers obtained by dividing the elementary quantum 4·77 by small integers, the deviation being well within the limits of the accuracy of observation.* The fact that these integers are small is to be emphasized. Compare Table I.

TABLE I.

Maximum for	K.	ϵ/N.	% error.
$\epsilon=0{\cdot}2534 \,.\, 10^{-10}$	5·30	4·77 : 19 = 0·251	0·956
$\epsilon=0{\cdot}5242$	4·61	4·77 : 9 = 0·53	1·094
$\epsilon=0{\cdot}674$	1·97	4·77 : 7 = 0·6814	1·086
$\epsilon=0{\cdot}937$	1·95	4·77 : 5 = 0·954	1·782

Even by means of the Q-curve (fig. 1) further maxima are noticeable at the points

0·30	(corresponding to	$0{\cdot}2981 = \frac{\epsilon}{16}$)
0·36	(,,	,, $0{\cdot}3669 = \frac{\epsilon}{13}$)
0·3975	(,,	,, $0{\cdot}3975 = \frac{\epsilon}{12}$)
0·45–0·46	(,,	,, $0{\cdot}4542 = \frac{2\epsilon}{21}$)
0·79–0·795	(,,	,, $0{\cdot}795 = \frac{\epsilon}{6}$)
1·20–1·30	(,,	,, $1{\cdot}1925 = \frac{\epsilon}{4}$)
1·80–1·90	(,,	,, $1{\cdot}908 = \frac{2\epsilon}{5}$)
2·30–2·40	(,,	,, $2{\cdot}385 = \frac{\epsilon}{2}$)

For an exhaustive discussion of the foregoing as well as for the *confirmation by means of the linear theory of errors* of the remarkable conformity to order, reference may be made to *Zeitschr. f. Phys.* xxxi. pp. 564–567 (1925).

Fig. 6 illustrates the brilliant agreement between theoretical and experimental integrals of error.

That this conformity does not result from the particular chance circumstances surrounding König's arrangements for his experiments, but that it possesses objective value, follows from the fact that the same results appear not only for König's observations on mercury in CO_2, but also for the entirely independent experiments of Radel.

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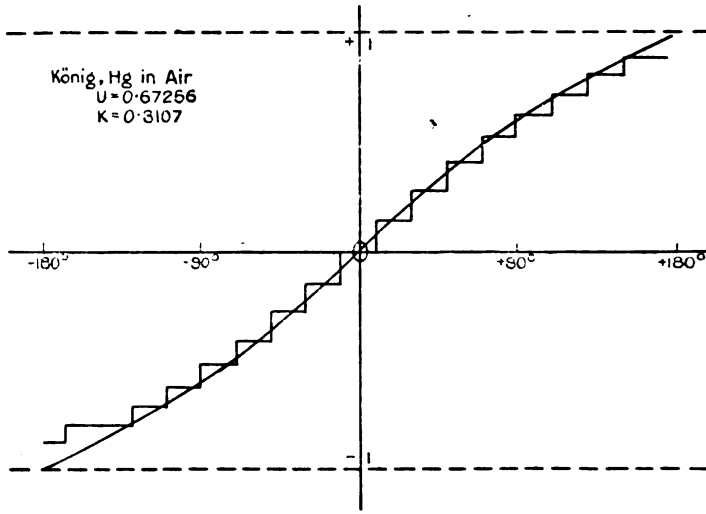
Fig. 6.



Summary of the results.—The assumption that the sub-electrons may be represented in the form $\frac{m}{n}e$, where n is not large and $m < n$, possesses greater probability than any *other assumption.*

Conclusions may be drawn in either of two directions. If the observations of shortages of the elementary quantum of electricity are to be reconciled with the proof for the existence of such a quantum, then it must be possible in some manner to refer these shortages to $4{\cdot}77 \,.\, 10^{-10}$ E.S.U. The fact that the apparently irregular shortages stand in the above mentioned relationship to $4{\cdot}77 \,.\, 10^{-10}$ E.S.U. can perhaps be useful in this connexion.

Another conclusion, however, is forced upon us as being at least equally probable: namely, that for small radii a division of the electron actually occurs, and in n parts. Of these n parts, m ($< n$) can occur as united *.

I have to thank Dr. phil. Frederick Doermann of Washington for his great kindness and trouble in translating this article from German into English.

Hamburg 23, May 11th.

* F. Ehrenhaft expressed this supposition as early as 1913; *cf.* F. Ehrenhaft, *Verhandl. d. Deutschen Phys. Ges.* xv. p. 1201 (1913), and his remarks in discussion of my paper at Innsbruck, *Phys. Zeitschr.* xxv. pp. 629–630 (1924).

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LXVIII. *Absorption of Light by Vapours of* Pb, Sn, Bi, Sb, *and* Mg. *By* Prof. A. L. Narayan, *D.Sc., F.Inst.P., and* K. R. Rao, *M.A., Madras University Research Scholar* *.

[Plate XXIII.]

Abstract.

Absorption of light by non-luminous vapours of Pb, Sn, Bi, Sb, and Mg has been studied, and it has been found that the absorption spectrum of lead shows, besides the fundamental line λ 2833, a banded spectrum at about 1100° C., degraded towards the red and spaced at intervals of 32 Å.U. nearly. Absorption spectrum of tin showed only a faint reversal of λ 2706·6. That of bismuth showed, besides λ 3067, 2524, 2276, and 2230 & 28, a typical banded spectrum containing about 20 bands. The absorption at each of these bands is very diffuse and complex, consisting of a number of finer bands. With increase of vapour density all these bands gradually fuse together (beginning from the short wave-length side) to form a region of continuous absorption. At about 1200° C. another typical banded spectrum appeared in the visible region extending from λ 6500 to λ 4500. The absorption spectrum of antimony showed fine lines at 2312 and 2306 and a banded spectrum extending from λ 2305 to λ 2250, while at higher temperatures there was another banded spectrum in the region 2830→3090 and a fine line at λ 2770. The existence of the banded spectra in the case of these metals of the higher groups of the periodic table leads us to the conclusion that the molecules of these elements are polyatomic. λ 4571, the single line spectrum of magnesium, has been for the first time photographed as an absorption-line by using a long column of the vapour.

During the past few months the authors have continued their studies on the absorption of light by vapours of different metals. It is the purpose of the present paper to give an account of the absorption spectra of Pb, Sn, Bi, Sb, and Mg.

No line series have been found in the spectra of the metals of IVth and Vth groups of the periodic table, nor is there anything known of the lines appearing at low voltages, as it is found very difficult to determine directly the critical potentials of such highly refractory elements. McLennan † has investigated the absorption spectrum of Pb and found that there was well-marked absorption at λ 2833 and λ 2170, and

* Communicated by Prof. A. W. Porter, F.R.S.

† McLennan and Zumstein: Roy. Soc. Canada, Trans. xiv. Ser. 3, Sect. 3, pp. 9–17 of 1921.

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that no absorption was indicated at 10291 as shown by the resonance potential of the elements. Foote and Mohler * have pointed out that an isolated group of infra-red lines observed by Randall by thermopile measurements falls within this region. J. J. Dobbie and J. J. Fox † have studied the absorption of light by vapours of As, P, Bi, and several other metals up to 3100, and found there were no traces of any kind of selective absorption in the case of As, P, and Bi. Recently Grotrian ‡ has published an account of his experiments on the absorption of light by vapours of these and some other metals. In all these experiments, the investigators used an absorbing column of metallic vapour maintained in a quartz tube heated electrically by a coil of nichrome ribbon. In the present experiments the authors used a charcoal furnace through which a powerful blast of air was maintained, to avoid any possible magnetic effect on the absorption lines, and the metal was enclosed in vacuum in an iron tube furnished with quartz windows. The absorption tube is exactly similar to the one used by the authors § previously and in their experiments on Thallium Vapour.

In all these experiments Kahlbaum's pure metals were used.

Fig. 1 represents the absorption spectrum of Pb at 1100° C.
Fig. 2 „ „ „ Bi; *a*, *b*, *c*, *d* being the photographs taken at gradually increasing vapour densities, *d* being the photograph at 1250 showing the banded spectrum in the visible region (Pl. XXIII.).

The absorption spectrum of Sb at 1150° C. has also been obtained. Owing to the low intensity of the carbon arc in this region, a good negative cannot be obtained.

The absorption of $1S-2p_2$, the single line spectrum of magnesium, has been obtained, but the photograph will not stand reproduction.

Lead.

The absorption spectrum of lead shows the asymmetrical nature of the fundamental line, λ 2833 being sharply defined on the short wave-length side, and with increase of temperature gradually spreads towards the other end. This line

* 'Origin of Spectra,' p. 65.

† Roy. Soc., Proc. xcviii. pp. 147–153, Nov. 3, 1920.

‡ *Zeits. f. Physik*, xviii. 3–4. pp. 169–182 (1923).

§ Phil. Mag. May 1923; and "Absorption of Lithium Vapour," Proc. Roy. Soc., Sec. A, July 1924, and "Absorption and Dispersion of Tl Vapour," recently communicated to the Royal Society of London.

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obviously corresponds to the normal state of the atom and is probably the first of the series.

At about 1100° C. the vapour shows a faint banded spectrum, which has not been described previously, extending from 3100 to 3400. At still higher temperatures these bands become stronger and wider. The approximate wave-lengths of the band heads are as follows :—

3352·3 Å.U.	3230·2 Å.U.
3321·5 „	3204·1 „
3290·0 „	3175·0 „
3260·0 „	3140·3 „

By using spark under water between two copper electrodes as the source of light, the authors found the vapour absorbed 2577, 2613, and 2614. Owing to the very low intensity of these absorption lines, these could not be successfully reproduced in the positives.

Tin.

The absorption spectrum of this element showed a faint reversal of the line λ 2706·6. No absorption was obtained at λ 3009·2 and λ 2863·4 as indicated by Grotrian, probably due to the fact that sufficiently high temperatures could not be obtained.

Bismuth.

The spectrum of this element shows besides the "raie ultime" λ 3067 a typical banded spectrum extending from λ 2600 to λ 2900 Å.U. This banded spectrum is degraded towards the red and is spaced at intervals of about 15 Å.U. We have succeeded in photographing 20 of these bands. The absorption at each of these bands is very diffuse and complex, consisting of a number of finer bands. With increase of vapour density all these bands gradually fuse together (beginning from the short wave-length side) to form a region of continuous absorption. To find if there are any absorption lines in the region covered by the banded spectrum, photographs were taken at gradually increasing densities. A careful examination of the absorption spectrum at about 800° C. shows that at 2721·5, 2730, and 2745 there are fine absorption lines probably not in any way connected

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with the banded spectrum. With the dispersion available, though the wave-lengths of the fine lines composing the bands could not be accurately measured, the approximate wave-lengths of the band heads have been determined and are as follows :—

2855·9 Å.U.	2744·8 Å.U.
2842·9 „	2732·6 „
2828·2 „	2722·0 „
2813·5 „	2712·3 „
2799·8 „	2701·9 „
2785·0 „	2693·2 „
2772·7 „	2681·5 „
2759·6 „	2670·0 „

At about 1200° C. another typical banded spectrum appeared in the visible region extending from about λ 6500 to λ 4500. The interval between the band heads varies approximately from 90 Å.U to 35 Å.U. as we go from the red end to the violet end. These bands show a distinctly fine structure. These bands also become stronger and wider with increase of temperature. But temperatures sufficiently high to develop these bands could not be obtained. Fig. 2 *d* shows the banded spectrum in the visible region at about 1250° C. At this temperature the transmitted light was light violet in colour. By using spark under water between two stout copper electrodes as the source of light, the authors found that at 900° C. the vapour absorbed 2524, 2276, 2230, and 2228.

Antimony.

The absorption spectrum of this element shows fine lines at λ 2312 and λ 2306 and a banded spectrum on the short wave-length side of these lines extending from 2305 to 2250 with a constant interval of 15 Å.U. nearly. The line λ 2312 is probably the same as λ 2313 noticed by Liveing and Dewar as a reversal line in the arc. At higher temperatures continuous absorption begins from the short wave-length side and extends into this region. As the temperature was raised still further the absorption spectrum

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showed another banded spectrum in the region λ 2830→3000 and a fine line at λ 2770.

The existence of the banded spectra in the case of these metals of the higher groups of the periodic table leads us to the conclusion that the molecules of these elements are polyatomic.

Magnesium.

The absorption spectrum of this element at high temperatures clearly shows λ 4571, $1S-2p_2$, the single line spectrum of the element which McLennan * was not able to observe. But the fact remains that this line appeared only at high temperatures, although one would expect from the quantum theory that this single line spectrum of the element should be first absorbed by the non-luminous vapour of the metal.

Our thanks are due to Messrs. G. Subrahmanyam and D. Gunniah, of the Department, for the assistance they have given in taking the photographs.

Research Laboratories,
H.H. The Maharajah's College,
Vizianagrum.

Note added in Proof, June 20th.—Since these results were communicated, further experiments have been conducted in this laboratory on "Fluorescence and Channelled Absorption of Bi Vapour," the results of which were published in a recent number of the Royal Society. Prof. McLennan and his collaborators have recently studied the arc reversals of Pb and Sn with a fluorite spectrograph (Roy. Soc. Canada, Trans. xviii. Sect. 3, 1924, pp. 57–75 & 77–78).

* Roy. Soc. Proc. vol. xcii. p. 574 (1916).
Absorption of this line, 4571, was consistently observed by the authors in their experiments on magnesium vapour, and the fact was communicated to the Astrophysical Journal, in a short note, on account of the considerable interest that centres round this line. But we have now succeeded in photographing this line, and therefore this portion also is included in this paper.

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LXIX. *The General Nature of Band Spectra.* By J. W. Nicholson, *M.A., D.Sc., F.R.S., Fellow of Balliol College, Oxford* *.

THE present paper proposes to suggest, in an introductory manner, the mathematical relation between band and line spectra. Following on the investigation of Curtis †, the theory of band spectra has recently received much development, and their origin, in the light of the quantum theory, is at least partially understood. Investigations have so far been restricted to an analysis of the spectral effect of the rotations of the molecule as a whole, constituting a special case of the quantization of the motions of a system containing more than one nucleus, but a case worked out in strict accordance with the opinion, now generally held, that a band spectrum can only arise from a system of a non-atomic, or at least doubly-nuclear structure. In a later paper, the analytical treatment, at least in an approximate manner, of the motions in a molecule which are consistent with less special motions of the nuclei, will be developed, with the type of spectral formula for bands to which it leads. At present we confine attention to a general account of a formula which appears to be capable of supplying the link between band and line spectra, with the consequent suggestion of the meaning of the appearance of Rydberg's constant in the former—as in Fowler's investigation of the band spectrum of Helium, where alone it has appeared hitherto in the precise manner of series spectra—and the manner in which its mode of occurrence may be looked for.

We must, in the first instance, review the main properties of band spectra in their many ramifications of type, as deduced entirely from the experimental side, with suggestions, at various points, as to the probable theoretical significance, on the lines of the quantum theory, of the complex phenomena which they present. Deslandres, to whom so much of the empirical work on band spectra is due, would apparently still regard a band spectrum as a possible emission from atoms, but if we accept the principles of the quantum theory of emission in their entirety, this possibility disappears—as can, in fact, readily be shown analytically—and we are compelled to regard even the band spectrum of Helium as due to a temporary molecular association of Helium with itself, or Hydrogen, which exists under the conditions effective in a vacuum tube during the passage of a discharge.

* Communicated by the Author.

† Proc. Roy. Soc. A, ciii. (1923).

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Band spectra appear most usually when the source is only feebly excited, and tend to disappear with a further excitation strong enough to develop the line spectra, although there are certain exceptions, as, for example, the band spectrum of Helium, and at least certain portions of the secondary spectrum of Hydrogen which are probably of a banded type—the "lines" not showing a normal Zeeman effect. In a case like Helium, where any excitation at all is necessary to form temporary molecular aggregates which can exist for a sufficient time during the discharge to develop a characteristic spectrum, it may well occur that a stronger excitation may be capable of developing and maintaining more complex aggregates, with a consequent actual increase in the intensity of some of the bands from such sources. Hydrogen, again, is known to form the aggregate H_3 molecule, but under conditions not very clearly defined. It is possible that this and others require a specific degree of excitation and consequent ionization for their optimum production. Many of the extremely weak lines in the secondary Hydrogen spectrum may proceed from such origins of a temporary kind.

Deslandres, in 1887, proposed that all band spectra should be represented by the very general formula

$$n = f(m^2p^2)s^2 + Bm^2 + \phi(p^2),$$

where n is the wave-number of the line in a band, (m, s, p) are integers, and f, ϕ quite arbitrary functions, but B constant throughout the band. At the same time, (f, ϕ), though arbitrary, were expected to be comparatively simple functions. Generally speaking, after the manner of use of this formula, it might be said that a band spectrum was viewed as a network of lines whose wave-number intervals formed three sets of arithmetic progressions, determined, at least approximately, by three integers. In other words, it was presumed that f and ϕ were effectively quadratic functions only, in m or p. A consequence is that the spectrum can usually be subdivided into sets of lines following formulæ of the simple type

$$n = A \pm Bm^2,$$

though it is now more usual to require the type

$$n = A \pm Bm \pm Cm^2.$$

Deslandres subsequently put forward the simpler formula

$$n = A + B(m+\alpha)^2 - C(r+\beta)^2,$$

where m and r are integers, as representing the positions of

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the "heads" of a complete band, where B and C are both necessarily positive.

As regards the general effectiveness of this formula, the following classical instances will suffice :—

(1) The "Swan" spectrum of Carbon is given by

$$n = 11{\cdot}64(m+0{\cdot}83)^2-19{\cdot}60(r+0{\cdot}03)^2+2407,$$

where m ranges from 63 to 69, both inclusive, and r from 45 to 53 inclusive.

(2) The first group of Cyanogen bands satisfies :

$$n = 12{\cdot}90(m+0{\cdot}6)^2-8{\cdot}60(r+0{\cdot}8)^2-974,$$

with m ranging from 73 to 79 and r from 56 to 66.

(3) The first group in the spectrum of Nitrogen is given by

$$n = 22785{\cdot}1+14{\cdot}6815(m+0{\cdot}5)^2-15{\cdot}1595r^2,$$

with m ranging from 34 to 48 and r from 37 to 53.

The first formula is due to Jones and Watts, the second to Fowler and Shaw, and the third to Deslandres.

The actual number of band spectra which have been thus represented by three parameters is about 17. It is of interest to note the number of individual band-components thus taken account of, which in the preceding cases is as follows :—

Case 1, 63 ; Case 2, 77 ; Case 3, 255.

So that it is quite clear that this simple Deslandres's formula is very frequently a close approximation to the actual laws.

The first comment which the quantum view of spectra must suggest relates evidently to the large values of the integers concerned. On this view, an integer occurring in a spectral formula means, of necessity, that some possible motion of a system, or a part of it, has been quantized, and that if the motion can be defined by a generalized coordinate q, the phase integral of the momentum with respect to q is the product of Planck's constant h and the integer concerned. We are not, at this point, necessarily supposing that the motion is of the type ordinarily called "pseudo-periodic," in that the coordinate q repeats itself in a specific period with no necessary relation to the periods of repetition of other coordinates which, in the Lagrangian sense, are formally independent of q in an analytical manner. Yet, of course, it may be contended that the analytical formulation

$$\oint p\,dq = nh$$

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is, at present, our only basis for the introduction of integers by the quantum theory, and that all spectra which are functions of integers necessarily proceed from pseudo-periodic motions to which this mode of formulation can alone apply—even if, by our failure to separate the variables in Jacobi's sense, such motions cannot be found, or even shown to exist, except in the simplest cases. The existence, as shown by the late Sir George Darwin and others, of the so-called "periodic orbits" in cases of the problem of three bodies as it occurs in astronomy, with variables completely unseparable by any known analytical method, is, in our view, a sufficient indication that such orbits must be presumed to exist in any problem of a set of moving gravitational masses (or electrical charges, such as nuclei and electrons) which can retain a configuration appropriate for a continued existence in the form of the "steady states" necessary for a consideration, by the quantum theory, of emission spectra, and that such states are required by the mere existence of such spectra.

Certain suggestions towards the generalization of the phase-integral specification have occasionally been put forward, but, if the preceding argument be granted, it would seem that there is no necessary generalization, but only the recognition that pseudo-periodic motions exist even if they cannot be determined exactly, and that any radiating atom or molecule is necessarily passing between two such states, which are the only possible configurations for an atom or molecule not temporarily subject to radiation or absorption of energy. We are implying, in other words, that the formulation

$$\oint p\,dq = nh,$$

which, in the hands of W. Wilson, Sommerfeld, and others, has been completely effective in interpreting extreme detail in all cases where Jacobi's analytical method is applicable, remains the final generalization which regulates the dynamics of the atom or molecule, and that, for example, if we could find a suitable analytical procedure, it would be equally effective in giving a strict numerical interpretation of the arc spectrum of Helium.

The large integers involved in the representation of band spectra, according to this view, presuppose motions in the emitting system which involve enormous multiples of h in their phase integrals. We only need to consider the simple

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hydrogen atom in order to show that they cannot be motions which appreciably depend on the outer electrons.

Any system containing an electron on its outer "rim," if that electron participates essentially in a motion of quantum number 50, must have a general "radius" comparable with 2500 times that of a Hydrogen atom—which is a quite impossible value. If τ is the quantum number and m the moving mass, the radius is of order determined by $\frac{\tau^2}{m}$. If, however, the moving mass is a nucleus, of mass comparable with M, that of a Hydrogen atom, this is at once reduced to a relative order

$$\tau^2/1830m,$$

and a number like $\tau=50$ has no effect on the order of magnitude of the distance between nuclei in a molecule, and consequently does not affect the order of magnitude of the molecular radius.

The conclusion is almost irresistible that such large integers constitute an effective proof that the motions of nuclei in molecules are to be quantized like those of electrons, and that such a procedure does not violate the restrictions to the radius of emitting systems which are imposed by other physical considerations.

Moreover, while, on the quantum theory, there is a severe limitation to the possible integers, dependent on the pressure of a gas, in its atomic state emitting a line spectrum, no such restriction operates in the case of a band spectrum. It is clearly possible, in a quantitative manner, for even a thousand members of a band to be shown without any interference with the size of the molecule which the pressure imposes.

Such a supposition is, of course, inherent in the work which has been done on band spectra arising solely from rotations of a molecule as a whole. The preceding argument shows that it is quite general when the nuclei are allowed to move in any manner consistent with the pseudo-periodic type of motion and the quantizing principle in its ordinary form.

If band spectra are subject to the quantization of nuclei, it follows that no band spectrum contains any new absolute constant of nature not already inherent in line spectra. Apart from the fine structure of the latter, determined solely by the relativity correction for a moving mass, this implies that the universal constant of bands is still that of Rydberg only, though, at present, it has only been demonstrated in the case of Helium.

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The only writer who, till recently, attempted to obtain a universal form of relation between band and line spectra was Halm *, who gave, on purely empirical grounds, a formula of some significance, capable of including, on the one hand, line spectra and, on the other, band spectra, as limiting cases. Its significance, at the time of its development, really lay in the fact that it provided bands with a "tail" as well as a head—a phenomenon which actually occurs in certain cases. Further knowledge of band spectra has not confirmed the *type* of formula suggested by Halm, but his investigation is still classical as the first definite essay towards a relation between spectra of the two forms. Recent knowledge has only served to enhance the fundamental importance of a somewhat neglected memoir.

We have already said that the first connexion between line and band spectra, in an ultimate sense which brings theory into play—though itself founded on a purely experimental study,—was due to Fowler in 1915. Fowler showed † that in the special case of Helium bands (now believed generally to be due to a temporary Helium compound or molecule), the "heads" satisfied a formula of the Rydberg type—not very accurately, but effectively if the Ritz or Hicks modifications of Rydberg's formula were used. These heads are doublets, and Nicholson ‡ showed later that the separations in wave number of these doublets vanished at the limit of the series, so that the series obtained by Fowler were "Principal Series" in the strict sense of line spectra. Although the details of the bands have been discussed further by Curtis, it is not yet possible, on the basis of this spectrum alone, to develop a composite formula which shall exhibit the whole band spectrum in a formula of the type Halm attempted to obtain, which will indicate the precise nature, from the point of view of atomic theory, of the constants involved.

But we may argue from the Helium band spectrum, which in many respects is quite a typical one, to other band spectra, and we may conclude with some certainty that the Rydberg constant is, in fact, present in all band as well as line spectra, though not necessarily in the simple and strictly analogous manner in which it occurs in line spectra. We may, indeed, go further, and say that if the "heads" of the bands—not always directly visible as strong parts of the bands, and often only calculable when the appropriate

* Trans. Roy. Soc. Edin. 1895.
† Proc. Roy. Soc. A, xci. (1915).
‡ Proc. Roy. Soc. A, xci. (1915).

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mathematical representation of the band has been previously elucidated—were known, they might be expected always to obey a Rydberg type of formula suitable for the heads as members of a line spectrum. Uniformity in physical phenomena would alone preclude any uniqueness regarding the heads of such a typical band spectrum as that of Helium.

Since the constant in the series formula for the Helium band heads is N, that of Rydberg, the principles of the quantum theory compel us to suppose that, whatever be the emitting system, it is one in which one electron is more remote than all the others. It would, therefore, be expected that this spectrum should be subject to the Zeeman effect—a matter in urgent need of test. For such a test would be a strong confirmation of the essential correctness of the quantum theory even in its predictions of the existence of "4N" and "9N" series in atomic systems which have lost two or three electrons respectively while one is returning. If molecular structures, as we may expect, are capable of similar losses, it is necessary for the returning electron to be very remote compared with others—the molecule thus behaving roughly towards this electron as a charged atom might do,—in order that a whole number multiple of Rydberg's constant should determine the spectrum as an external multiplier.

Otherwise, if the electrons all remain at similar distances from the nuclei in the initial and final stationary states, no such simple multiple can be expected. As an illustration, it is sufficient to consider an *atom* with a single nucleus νe and n electrons *in a ring*, which passes to another ring.

The spectrum, in wave number, is

$$n = \mathrm{N}(\nu - \tfrac{1}{4}\mathrm{S}_n)^2 \left\{ \frac{1}{\tau_1^2} - \frac{1}{\tau_2^2} \right\},$$

where τ_1 and τ_2 are integers, and the multiplying constant is, not Rydberg's N, but

$$\mathrm{N}(\nu - \tfrac{1}{4}\mathrm{S}_n)^2,$$

which may be an incommensurable multiple. S_n, of course, is here the usual

$$\mathrm{S}_n = \sum_{\mathrm{S}=1}^{n-1} \operatorname{cosec} \mathrm{S}\pi/n.$$

Such incommensurable multiples are clearly to be expected in the usual band spectra, if due to molecules, for such molecules must contain many transitions between states in which —for both original and final states—no electron is less intimately associated with the nuclei than any other. In our

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view, it is almost probable that the search for Rydberg's constant in band spectra, except in peculiarly special cases, like that of Helium where it occurs without such a multiplier, has failed for this reason. But it would seem clear that the heads of bands in any such spectrum, if they are really the true "heads"—a matter sometimes in doubt,—should always follow a Rydberg type of formula,

$$n = N\alpha \left\{ \frac{1}{(\tau_1 + \mu_1)^2} - \frac{1}{(\tau_2 + \mu_2)^2} \right\},$$

where τ_1 and τ_2 are integers, and α is a purely numerical constant with a significance like that of $(\nu - \frac{1}{4}S_n)^2$ in the preceding discussion of atoms.

It is, perhaps, only necessary to add that, even for the purpose of preserving N as the constant of the ordinary arc spectrum of Helium, we have to suppose that, of the orbits of the two electrons in the neutral state, one is very much larger than the other.

We conclude, therefore, that incommensurable multiples of the Rydberg constant may be the prevailing factors in the majority of band spectra, and if these factors are elucidated and identified in simple cases, such as the band spectrum of Hydrogen, they give valuable knowledge in themselves as to the nature of the molecular configuration. Moreover, an ordinary Zeeman effect should only be expected when the constant is N itself.

We now return to the more descriptive portion of some of the phenomena characteristic of band spectra. The large integers are quite general, and it is rarely that any integer less than 30 is found. Deslandres, in fact, considers that the bands corresponding to small integers are usually in the unexplored part of the infra-red region.

If, to the preceding formula, we add a term to take account of the "degraded" part of the band, towards red or violet, the complete formula becomes

$$n = \pm A + B(m+\alpha)^2 - C(r+\beta)^2 \pm (s+\gamma)^2 f(m^2, r^2),$$

where all the coefficients are positive in known bands, and (m, r, s) are three integers. The coefficient $f(m^2, r^2)$ varies from one band to another, and is invariably very small, at least 50 to 200 times smaller than B or C.

Sometimes the term with B is absent, and sometimes that with C. For example, in the absorption spectrum of Oxygen,

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there are 5 bands, whose representative formula may be written as

$$n = 48788{\cdot}8 - 14{\cdot}112(r + 0{\cdot}2775)^2$$

$$(r = 46, 47, \ldots, 50),$$

without the additive term, and, on the other hand, Fowler has shown that the so-called "Fourth group of Nitrogen bands" has no coefficient C, but only the additive term. Moreover, only two or three values of one of the integers may appear.

The carbon monoxide spectrum, as shown in comets, for example, gives bands corresponding to seven values of r, but only two values of m. Instances of the converse, if less frequent, are nevertheless available, and there is no real distinction, on this basis, between the integers m and r in the nature of their occurrence in spectra.

Now the absence of any particular integer, or its mere restriction, for purposes of visual spectra, to a very limited number of consecutive values, should, on the general view we are developing in accord with the quantum theory of spectra, indicate only that the effective degrees of freedom of the stationary states of the molecule, associated with the bands, are restricted—perhaps by the physical conditions which prevail. This can easily be seen if we consider that such states must fall into distinct *types*, in which, on passing from one state to another—both being defined, as indicated previously, by pseudo-periodic motions,—no motion, or change of motion, takes place in certain coordinates, and no corresponding quantum numbers can therefore appear in the formula for the bands. Such motions are, in fact, so infrequent that at any time there cannot exist a number of molecules, in the region examined, effective for the production of a radiation capable of affecting a photographic plate. For example, if a molecule contains only two nuclei, sets of stationary states must ordinarily exist in which the arrangement continues to be symmetrical about the line joining the nuclei—as, in fact, in the purely rotational band spectra hitherto discussed,—and, in this eventuality, passage from one state to another only involves motion of nuclei along the line joining them, and not in their other degrees of freedom.

This is, of course, equivalent to a statement that such incomplete band spectra result from passages between molecular stationary states which belong to the "degenerate cases" of the general orbits, which are theoretically possible

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for a molecule under the fundamental quantum principle—which we consider to be the essential formulation,—that

$$\oint p\,dq = nh$$

for every degree of freedom of every electrical charge, *positive or negative,* in the molecule.

Again returning to the general descriptive formula of band spectra, we note that the functions $f(m^2, p^2)$ are very frequently constant—within the limits of experimental error,—especially if the starting-points of the integers m and r, which are never, by experiment, entirely determinate, are chosen suitably. This has been shown clearly by a somewhat fundamental investigation of Heurlinger *. We could, however, refer back even so far as to Moseley's classical investigation of the X-ray spectra of the elements, where an exactly similar mathematical difficulty appears. The leading lines of these spectra had wave numbers proportional to $(N-\alpha)^2$, where N increases from element to element by unit steps, and α is an incommensurable, and not small, magnitude. The *absolute* value of N cannot be determined by any experiment, and it remains as a magnitude which increases by unit steps, and can only, as now generally believed, be the atomic number, determined by nuclear charges of the element. But the absolute value of N has only been confirmed by the Bohr theory of the Hydrogen spectrum, according to which we know the absolute scale of measurement. Previous to the existence of this theory, Hicks and Rydberg showed independently that a better agreement with the experimental results, as they were then known, could be found by supposing the existence of elements with atomic weights between those of Hydrogen and Helium.

The difficulty thus defined continues to exist, however, in the case of the band-spectrum formula. No experimental information can be presumed to be sufficiently precise to allow a specification of the exact integer—in the quantum specification,—which really determines the wave-length of any component member, and only differences of such integers can be determined precisely. It follows that if a spectrum contains a term like $(m+\alpha)^2$, where m goes up in unit stages, the meaning and value of α are, at present, entirely undefined in any band spectrum. They change according to the value of m adopted, and, in this respect, Heurlinger's investigation

* Dissertation, Lund, 1918.

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is strictly parallel to those of Rydberg and Hicks to which we have referred. And, at this point, the formula for band spectra, as a function of integers, becomes analogous to that for line spectra as originally given by Rydberg, who contended that the line spectra did not depend on integers, but on expressions of the form $(m+\mu)$, where m is an integer and μ an atomic constant whose nature could not be elucidated without an atomic model—with the consequence that the absolute value of m was also indeterminate.

We propose to suggest, leaving analytical treatment of the theoretical basis for a further paper, that the general formula for band spectra is of the type,

$$n = \mathrm{N}' \left\{ \frac{1}{q+\mu+\alpha(m+\alpha_1)^2+\beta(r+\beta_1)^2+\ldots} \right\}^2 - \mathrm{N}' \left\{ \frac{1}{q'+\mu+\alpha(m'+\alpha_1)^2+\beta(r'+\beta_1)^2+\ldots} \right\}^2,$$

where N′ is a Rydberg constant, modified or not by a purely numerical multiplier; and (q, q', m, m', r, r') are integers. It is also presumed that $(\alpha_1, \beta_1, \ldots)$ are at least approximately constants as regards the varying integers, and that the coefficients $(\alpha, \beta, \ldots)$ are very small and dependent on the ratio m/M of the mass of an electron to that of a typical nucleus in the molecule.

The integers (q, q') arise as in the ordinary quantum theory applied to electronic orbits, but (m, m', r, r') are integers arising from the quantization of degrees of freedom of the nuclei. This, of necessity, confines the actual motions of the nuclei to a range dependent on m/M in comparison with the range of electronic motions, and the effect is therefore a multiplication of such a factor into any terms of the formula which involve these integers.

It is, of course, only contended that this is the appropriate first approximation to the true formula in exactly the same sense and with the same physical significance as Rydberg's form is the first approximation to line spectra.

From the smallness of α and β, a binomial expansion of the formula is possible in powers of $(\alpha, \beta, \ldots)$, and it follows that if (q, q') are kept constant, a Deslandres formula ensues approximately for passages between states characterized by variations only of the quanta inherent in nuclear motion. Moreover, a band head corresponds to specific constant values of the nuclear integers, and all the heads, as (q, q') vary, form a Rydberg line series. The formula, in fact, appears to conform to all the present existing knowledge of series relations.

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In view of the preceding argument regarding the smallness of $(\alpha, \beta, \ldots)$ it is very significant that bands due to the lighter elements are represented with much greater difficulty by a Deslandres formula, and, in fact, in the Fulcher bands of Hydrogen—the element for which m/M is greatest—no such formula can be regarded as quite satisfactory. The meaning would appear to be that $\alpha^2, \beta^2, \ldots$ are no longer sufficiently negligible in the binomial development. Numerical investigation, which we do not consider it necessary to include in this paper, fully confirms this, and by retaining α^2 in the case of the Fulcher bands and in other spectra incompletely interpreted by Deslandres's simpler formula, we can find some of the constants if they are expressed in the new form suggested. The resulting values of α and q, in that form, are in all cases of the order of magnitude which would be expected for spectra given by such a formula in the visible region. This is a valuable confirmation of the type.

In conclusion, we may briefly indicate certain of the less general properties of some band spectra which theory must ultimately account for.

In the main, band spectra form three classes. Those of the first class fall off, or are degraded on one side only, red or violet, and come to a sharp end on the other side, with their head-differences arranged nearly in arithmetic progression, and the components associated with any head also so arranged. This group contains the majority of known spectra. In the second class, the heads degrade again on one side only, but the heads are not readily seen unless the dispersion is weak, and in other cases are in no respect outstanding and are perhaps not even visible. Some of the components of each band have, in this case, differences in arithmetical progression, but sometimes the differences are actually constant; other portions, again, may have no apparent order, although the individual bands of these components are precisely like the others. Secondary Hydrogen, in its lines which show no Zeeman effect, belongs to this class, and is probably the most difficult member to elucidate. Other cases are the band spectrum of Iodine, investigated by Hasselberg, and Croze and Birge's "first group of Nitrogen bands."

The third class of bands contains those which have no "heads" in the ordinary sense, but which degrade on both sides of the maximum intensity. These are found to follow a Deslandres formula on each side, reckoned from the maximum point as an origin.

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Bands are known with a constitution yet more simple, but these are, ordinarily, absorption-bands of very complex compounds. Perhaps the most noteworthy are the very extensive absorption spectra of sulphurous acid and of toluene. In the former case, Baly and Garrett* have succeeded in representing the band by the formula

$$n = 33751{\cdot}6 + 2{\cdot}73m + 223{\cdot}225\tau,$$

not involving the squares of the integers m and τ—but not thereby conflicting with the general suggestion of a formula we have made,—involving, in fact, very small α and very large α_1, but no more extensive modification. This is a case of equidistant components, and the band degrades on both sides. In actual fact, sulphurous acid also has a group of bands in the ultra-violet, and six more, found by Coblentz, in the infra-red. All may be included in the single formula with three integers (s, m, τ),

$$n = 2{\cdot}73m + 223{\cdot}25\tau + 192{\cdot}866s,$$

where m ranges from -44 to $+37$, n from -7 to $+13$, and

$$s = 5, 6, 7, 9, 13, 16, 175$$

—a very remarkable collection of integers. This formula can simultaneously represent 12,000 components. Baly and Garrett, in other papers, have applied certain quantum considerations to this band, but not, as we consider, in a form which is in accord with the general function of quanta in relation to spectra. At the same time, it is not to be presumed that such complicated and, if the term may be used, loosely-bound molecules as those of sulphurous acid necessarily behave in an analogous way to the simpler molecules with only two or three nuclei. It is noteworthy that all cases in which this simple type of law appears to be satisfactory appear to correspond to very complex molecules, as again in the case of toluene, and frequently to very unstable compounds like sulphurous acid, probably associated with water in a very large molecular aggregate. Such molecules provide, indeed, an extreme limiting case in one direction, and their study is not quite germane to our present object.

* Phil. Mag. xxxi. p. 512.

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LXX. *Notices respecting New Books.*

Tables Annuelles de Constantes et Données Numériques de Chimie, de Physique et de Technologie. Vol. v., part 1 [pp. xli. + 804]. (English agents: Cambridge University Press; 1925. Price not stated).

THE fifth volume of the well-known tables of constants published under the patronage of the International Research Council and of the International Union of Pure and Applied Chemistry covers the literature of the years 1917 to 1922 inclusive. The next volume to appear will deal with the years 1923 and 1924. The liquidation of the arrears of publication arising during the War period will then have been completed, and thereafter annual publication will be resumed.

The first part of the fifth volume, published recently, contains over 800 pages; the data given have been extracted from more than 400 scientific journals and publications, and many additional publications, not enumerated in the volume, have been searched for relevant data. These figures emphasize not only the enormous volume of scientific work published in these days, but also the impossibility of collecting complete observational data relative to any particular point without tables of reference such as those under review. No scientific library can afford to be without these volumes.

Full references to the original publications are given throughout. The Table of Contents, printed in French, German, English, and Italian, is sufficiently detailed to enable the particular section in which the data required are given to be easily found. Cross-references are given where necessary. Readers of this Magazine desirous of obtaining more detailed information about the Tables, with specimen pages, can obtain such on application to the General Secretary, Dr. C. Marie, 9 Rue de Bagneux, Paris (VI).

LXXI. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from vol. xlix. p. 1080.]

January 21st, 1925.—Dr. J. W. Evans, C.B.E., F.R.S., President, in the Chair.

Dr. LÉON W. COLLET, For.Corr.G.S., Professor of Geology and Dean of the Faculty of Science in the University of Geneva, delivered a lecture on 'The Latest Ideas on the Formation of the Alpine Range.'

In 1905 Prof. E. Argand determined in the Pennine Alps the existence of six great recumbent folds or nappes. He started from the notion of the geosyncline, so splendidly developed by Dr. E. Haug, and destined to remain for all time the basal conception of tectonics. His equipment included a very detailed stratigraphical knowledge, and, armed with this, he has succeeded in straightening out the recumbent folds, and in thus reconstituting

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the Pennine region at various stages of its development, when the general geosynclinal depression was subdivided by geanticlinal ridges.

On the base of Argand's results Dr. R. Staub found in the north-eastern part of the Swiss Alps the same tectonic elements, covered by six higher nappes belonging more to the type of the 'thrust-masses' of the North-Western Highlands of Scotland than to the type of the recumbent folds of the Pennine Alps. This new series of nappes has been named by Staub the Austrides, for they form the main part of the Austrian Alps.

For many years the Austrian geologists regarded the Tauern as a gneissic massif surrounded by schists and shales. Lately Prof. L. Kober, of the University of Vienna, has recognized instead a window: that is, a horizontal cut, due to erosion, in the nappes of the Austrides, which reveals deeper nappes belonging to the Pennine series. Therefore, this discovery shows that the nappes of the Austrides have been thrust over the Pennine nappes in the Austrian Alps, just as in the north-eastern part of Switzerland.

This was excellent, but a satisfactory co-ordination of the work done by Austrian and Swiss geologists was needed. That was accomplished at the end of last year by Dr. Staub. He published a memoir on the formation of the whole Alpine chain, from the French Alps to the Austrian, including the Swiss Alps, and summarized his views in a splendid geological map.

A capital point is the employment of Wegener's ideas on the drifting of continental masses, to explain the movement of the Hinterland towards the Foreland of the geosyncline. Foreland and Hinterland constitute the boundaries of the great Alpine geosyncline: together they recall the two jaws of a vice. Prof. P. Termier, Director of the French Geological Survey, has shown how the approach of the two jaws has led to the compression of the geosyncline, and thus to the development of the Alpine chain. Prof. Argand, at the Session of the International Geological Congress in Brussels, showed that the nappes of the Austrides belong to the Hinterland: that is, to Africa or Gondwanaland. Therefore the Austrides, with the Préalpes, represent a small part of Africa resting on Europe or Eurasia. These important views are accepted by Dr. Staub and by the Lecturer. Alpine tectonics are a great support to Wegener's theory on the drifting of continental masses.

The Lecturer presented the results arrived at, with the help of an enlargement of Dr. Staub's geological map, drawn by his Assistants for this lecture and others that he had arranged to give at the University of Cambridge, at the University College of Wales, Aberystwyth, and to the Geological Society of Edinburgh.

At the end of the lecture Prof. Collet showed lantern-slides with views of the Pennine Alps (to illustrate Argand's standard work) and views of the Mont Blanc Massif, where he has been working in recent years with his collaborators, Prof. Reinhard and Dr. Parejas.

[*The Editors do not hold themselves responsible for the views expressed by their correspondents.*]

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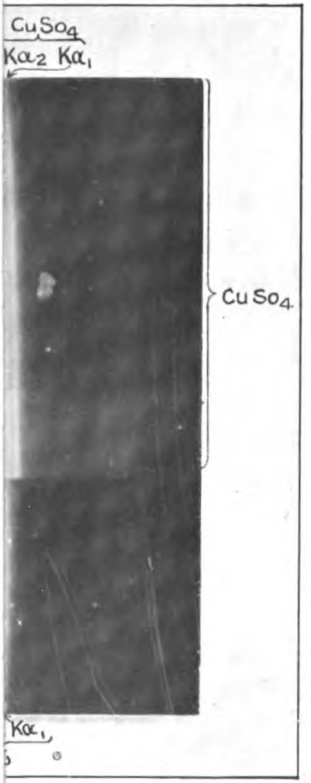

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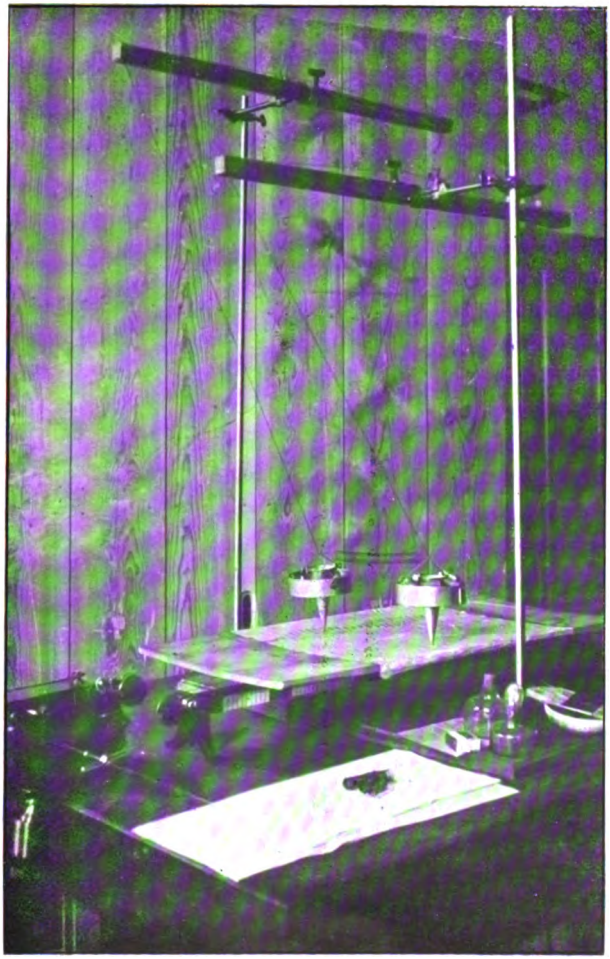

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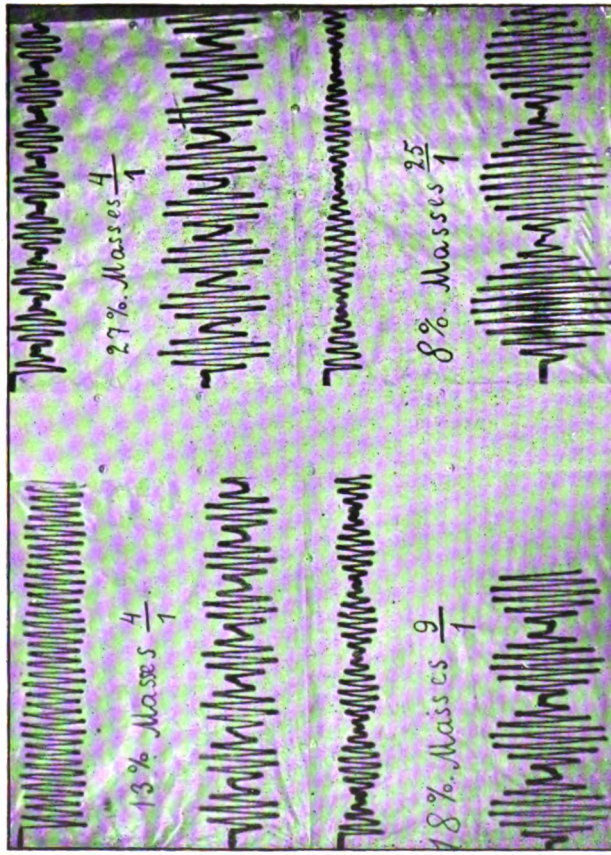

$m_1 = 2900$ g.
$l_1 = 49$ cm.

No. 1.

$m_2 = 725$ g.
$l_2 = 92$ cm.
$k = 3420 \frac{\text{d.}}{\text{cm.}}$

$m_1 = 2916$ g.
$l_1 = 49$ cm.

No. 3.

$m_2 = 324$ g.
$l_2 = 92$ cm.
$k = 1140 \frac{\text{d.}}{\text{cm.}}$

$m_1 = 2900$ g.
$l_1 = 49$ cm.

No. 2.

$m_2 = 725$ g.
$l_2 = 92$ cm.
$k = 9170 \frac{\text{d.}}{\text{cm.}}$

$m_1 = 2850$ g.
$l_1 = 49$ cm.

No. 4.

$m_2 = 114$ g.
$l_2 = 92$ cm.
$k = 1140 \frac{\text{d.}}{\text{cm.}}$

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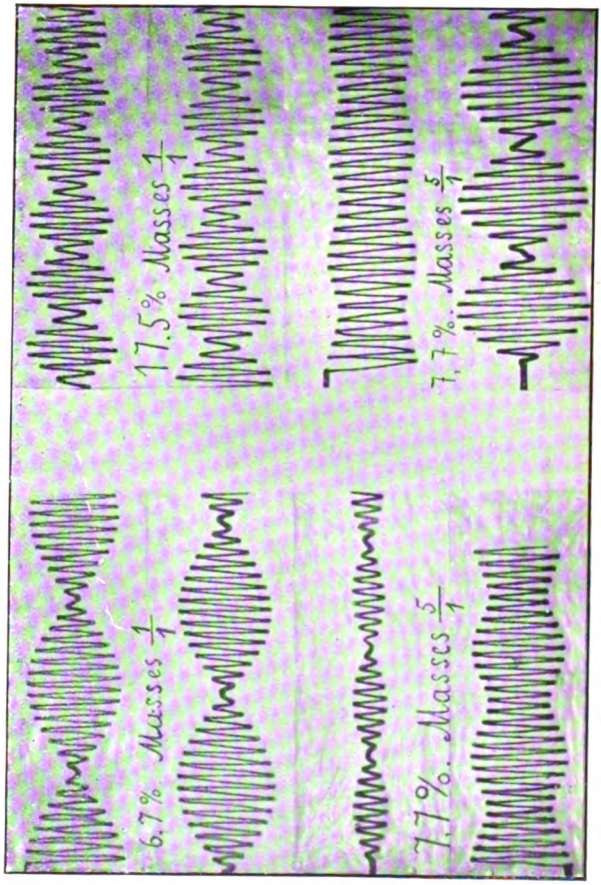

$m_1 = 1530$ g.
$l_1 = 93$ cm.

No. 5

$m_2 = 1530$ g.
$l_2 = 93$ cm.
$k = 1140 \frac{\text{d.}}{\text{cm.}}$

$m_2 = 2700$ g.
$l_2 = 93$ cm.

No. 7.

$m_1 = 540$ g.
$l_1 = 93$ cm.
$k = 1140 \frac{\text{d.}}{\text{cm.}}$

$m_1 = 500$ g.
$l_1 = 92$ cm.

No. 6.

$m_2 = 500$ g.
$l_2 = 92$ cm.
$k = 1140 \frac{\text{d.}}{\text{cm.}}$

$m_1 = 2700$ g.
$l_1 = 93$ cm.

No. 8.

$m_2 = 540$ g.
$l_2 = 93$ cm.
$k = 1140 \frac{\text{d.}}{\text{cm.}}$

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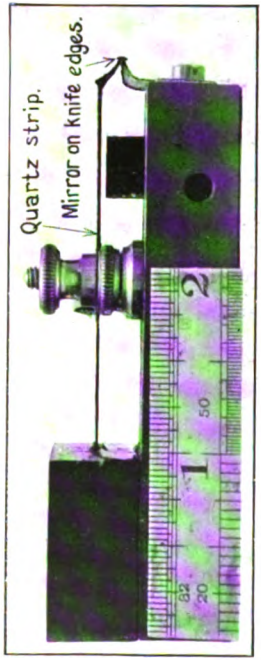
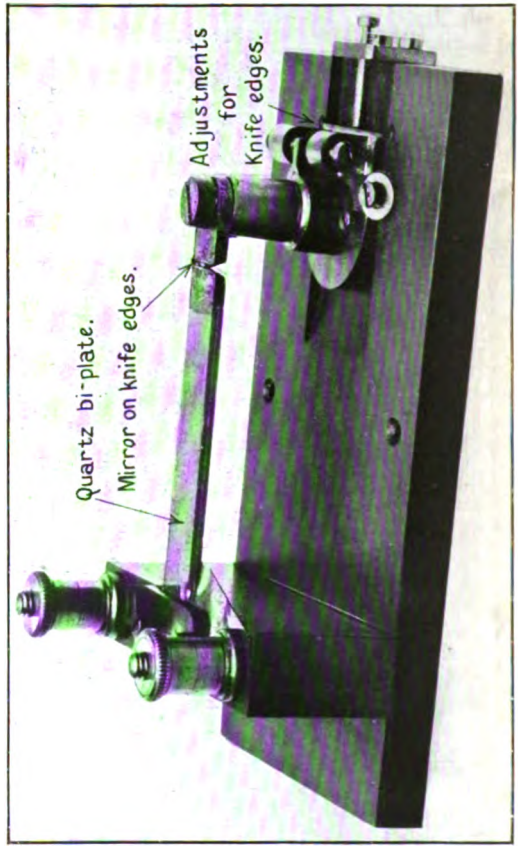
Fig. 3.



a. **Single-Strip Quartz Oscillograph.**



b. **Double-Strip Quartz Oscillograph.**

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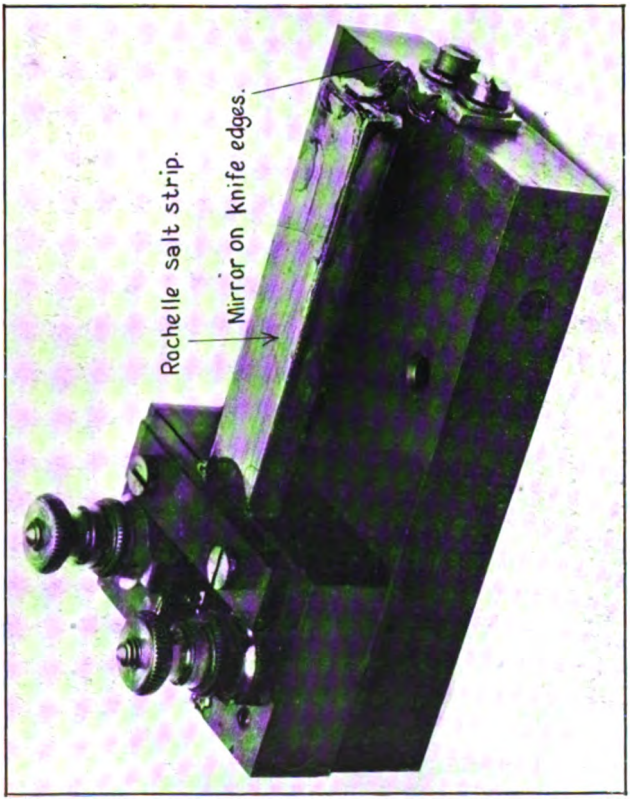

c. Single-Strip Rochelle Salt Oscillograph.

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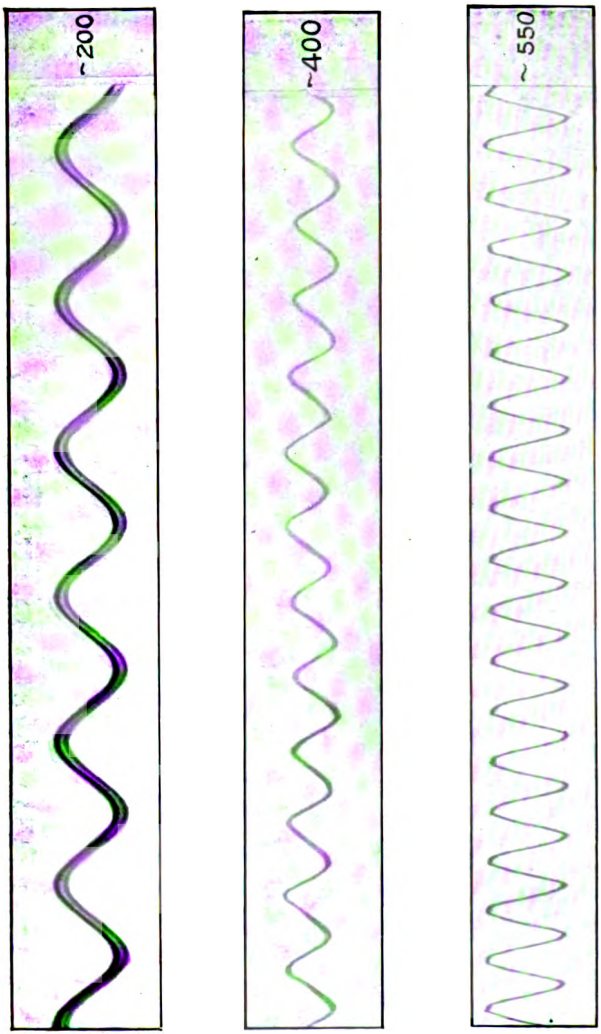
Fig. 4.



Tuning Fork ~200 Calibration.

Rochelle Salt Oscillograph (Single-Strip).

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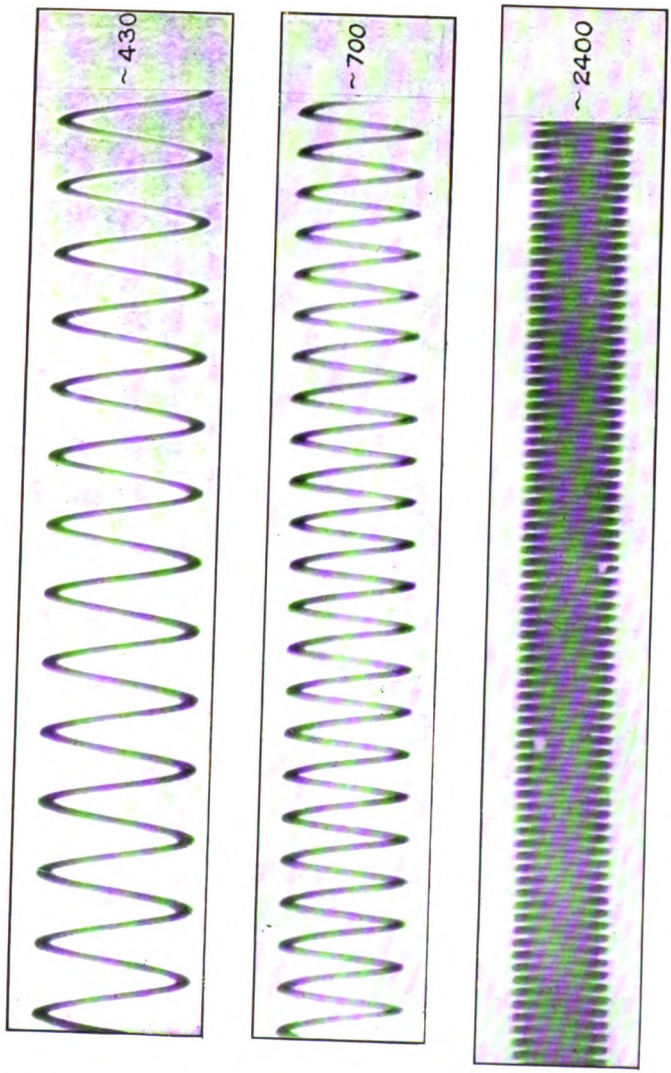

Piezo-Electric Oscillograph Records (using dropping-plate camera).

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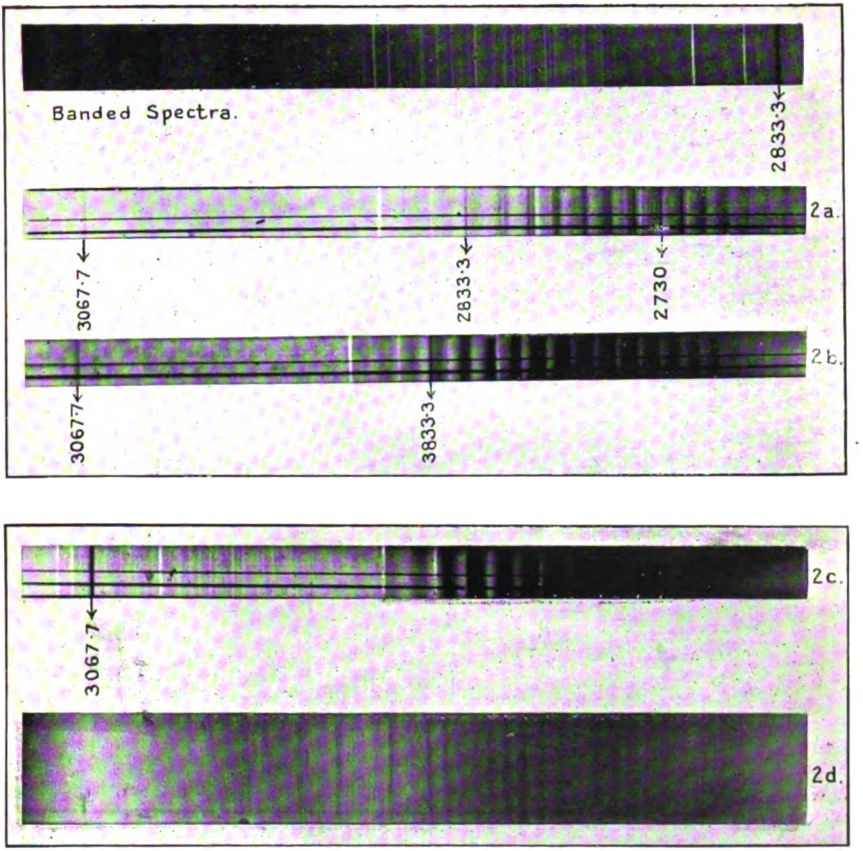

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